A REVIEW OF THE CONTAMINANTS AND TOXICITY ASSOCIATED WITH PARTICLES IN STORMWATER RUNOFF
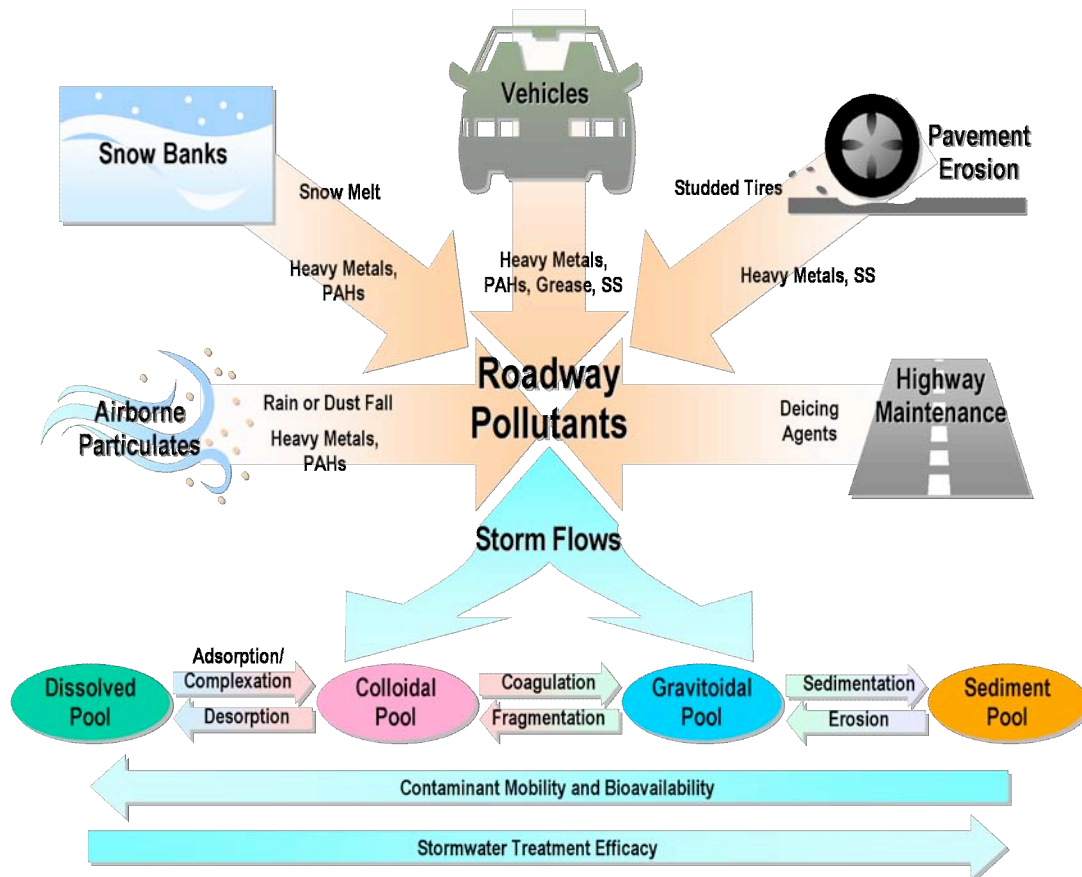

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CONTENTS

DISCLAIMER AND ACKNOWLEDGEMENTS

AVS	Acid Volatile Sulphides
BMP	Best Management Practices
ChV	Chronic Value
DOC	Dissolved Organic Carbon
EC	Effective Concentration
ESD	Equivalent Spherical Diameter
GPC	Gel Permeation Chromatography
HPLC	High Pressure Liquid Chromatography
IC	Inhibiting Concentration
LC	Lethal Concentration
LOEC	Lowest Observed Effect Concentration
MATC	Maximum Allowable Toxicant Concentration
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
NOEC	No Observed Effects Concentration
NPDES	National Pollution Discharge and Elimination System
NURP	National Urban Research Program
PAHs	Polyaromatic Hydrocarbons
PSD	Particle Size Distribution
RFE	Reverse Flow Elutriation
SEM	Simultaneously Extracted Metals
SF	Sequential Filtration
SPLITT	Split-Flow Thin Cell Separation
SVOC	Semi-Volatile Organic Carbon
SSA	Specific Surface Area
TIE	Toxicity Identification Evaluation
TFF	Tangential Flow Filtration
TL_{50}	Median Tolerance Limit
TMDL	Total Maximum Daily Load
UF	Ultrafiltration
UV	Ultraviolet Light
VOC	Volatile Organic Compound
WET	Whole Effluent Toxicity
μm	Micrometer or 10^{-6} meters

FIGURES

TABLES

Organic and inorganic contaminants in stormwater runoff can impair receiving water quality and disrupt ecosystem health. Efforts to reduce these impacts through the development and deployment of best management practices (BMPs) are hampered by an incomplete understanding of the role that particles play in the fate, transport, and toxicity of pollutants in roadway runoff. This knowledge gap stems largely from methodological limitations and inconsistencies among investigators in the way particles, contaminants, and toxicity are measured. The lack of agreed upon standard methods, and agreed upon standard terminology, is a barrier to BMP design, and creates uncertainty in the regulatory context where the impact of stormwater discharges must be quantified as part of the Total Maximum Daily Load assessment process.

The primary purposes of the report are to (1) document what is known about the relationship between particle size, pollutant levels, and toxicity in stormwater runoff from highway facilities, (2) critically examine existing methods for the collection of storm water samples and subsequent measurements of toxicity, heavy metals, organic pollutants, and particle size distributions, and (3) identify knowledge gaps that currently limit Caltrans' ability to mitigate stormwater pollution.

The common practice of separating particulate and dissolved contaminant fractions based on arbitrary size cutoffs (e.g., 0.45 μm) does not yield sufficient information needed for successful BMP design, including: (1) the partitioning of inorganic and organic contaminants between rapidly settling and non-settling particles; (2) the likelihood that contaminant-bearing particles will change size during treatment; and (3) the likelihood that contaminant-bearing particles will filter out during infiltration.

A promising alternative classification proposed by Gustafsson and Gschwend (1997) divides contaminants into dissolved, colloidal, and gravitoidal fractions based on the expected behavior of contaminants within each fraction. For example, if the majority of contaminants are associated with rapidly settling particles (gravitoidal fraction), then sedimentation basins may be a useful treatment approach. Contaminants dynamically transfer between fractions by coagulation, fragmentation, adsorption, complexation, and desorption. These dynamic phenomena should be considered, and ideally exploited, in BMP design.

Progress in the development of stormwater BMPs will depend on the degree to which the issues identified above can be resolved through focused research. Specific areas that need to be addressed through targeted research include:

1. Development and testing of methods for delineating the distribution of stormwater contaminants and toxicity between the dissolved, colloidal, and gravitoidal fractions. Ideally these methodologies would involve on-line instruments that can be deployed in the field.

2. Field studies aimed at elucidating how contaminant fractions evolve over time and space as they are mobilized by storm flows, interact with BMPs, transport through engineered or natural watersheds, and impact receiving waters.

3. Development of sampling and analytical methods for measuring the biological impact of stormwater contaminants on receiving waters and sediments.

4. Utilization of continuous particle measurement as a tool to substitute analytical monitoring and to determine the performance evaluation of BMPs.

The findings documented in each chapter are summarized below:

Chapter 2 Measurement of Particle Size Distribution in Roadway Runoff

∞ A large fraction of potentially toxic inorganic and organic compounds in roadway runoff is associated with particles, especially the colloidal fraction. Thus, to understand the role that particles play in pollutant transport, methods are needed to characterize the physical and chemical nature of particles, and how these properties change over the particle size spectrum. The size distribution of pollutants is also important in the design of best management practices for mitigating roadway runoff impacts on receiving waters.

∞ A wide variety of instruments are commercially available for particle size analyses, using one or more physical properties. Some of the physical phenomena exploited include electrical properties (such as differential resistance), transport properties in the case of sedimentation and hydrodynamic chromatography, and optical properties as represented by a wide variety of light scattering phenomena.

∞ Some particle size instruments detect and enumerate one particle at a time (e.g. single particle counters) while others analyze the sum of measured signals (e.g., Fraunhofer diffraction, light scattering) to obtain an ensemble average.

∞ Single particle counter instruments are capable of giving "absolute" concentrations in terms of the number of particles per unit volume, provided that the volume element is well defined and all particle classes can be detected. For example, light obscuration instruments are routinely used for on-line monitoring of water treatment processes [98,99].

∞ Ensemble average methods are generally not capable of giving "absolute" concentrations because the corresponding instruments do not yield particle concentrations on an absolute basis. However, they are generally faster than single particle counters, since they average all of the particles present in a sample, rather than counting each particle individually.   The single particle counters are also less subject to statistical variations arising from registering too few particles.

∞ A fundamental limitation of characterizing particle size distributions in roadway runoff is that no single approach can characterize the entire range of particle sizes

present. This limitation arises because: 1) no single instrument can sense the more than six orders of magnitude in the range of particle sizes present in storm water, from nanometer-sized colloidal organic material to millimeter-sized sand and silt, and 2) the physical properties of particles (e.g., density, roughness, fractal structure, etc.) are highly variable and subject to systematic biases (e.g., the physical properties of large and small particles can be different).

∞ Some particle sizing techniques are simple and do not require significant capital expenditure (e.g., sieving and manual microscopy), but these approaches tend to be highly labor intensive.

∞ Automatic or semiautomatic instrumentation is less labor intensive, but the instruments can be more costly. In short, there is no perfect particle-sizing instrument. The best instrument for any particular application should be selected based on the kind of information that is desired and any practical constraints that might apply. Many instruments also require pre-calibration. As with any analytical measurement, QA/QC issues should be carefully considered.

Chapter 3 Particle Fractionation

∞ Typically, pollutants are classified as either "dissolved" or "particulate" based on whether or not they pass through a 0.45 micron filter. The 0.45 micron division between dissolved and particulate phases has a long history in the field of aqueous geochemistry. However, the choice of a single cut-off is arbitrary when applied to samples of roadway runoff, because the particle size distributions extend continuously from tens of nanometers (e.g. hydrated metal ions) to hundreds of micrometers (e.g. suspended matter).

∞ There are several different approaches available for fractionating particles by size. Particles with length scales in excess of approximately 100 microns can be fractionated using conventional wet or dry sieving, typically with nylon sieves. Sequential filtration, thin-cell split flow fractionation, and elutriation can be used to fractionate particles in the size range of 1-100 microns. Gel permeation chromatography (GPC) in defined gel phases and sequential ultrafiltration (UF) can be used to fractionate the colloids smaller than 1 micron into classes based on size, mass, or electrical properties, to name a few.

∞ Chemical toxicology and physical characterization of a single particle size fraction typically requires about 1 gram of material. This constraint means that samples must undergo a significant concentration step prior to fractionation. For example; if 50 to 100 grams of solids are required for complete physical and chemical characterization of the fractionated sample, then approximately 50 to 10,000 L of roadway runoff must be analyzed.

Chapter 4 Particles and Toxicity in Roadway Runoff

∞ Particles influence chemical toxicity by contributing stress to test organisms, altering bioavailability, and modifying exposure level. Sampling and toxicity test methods used in most roadway runoff monitoring programs are not adequate to assess biological impacts related to particles in roadway runoff.

∞ Toxicity is frequently detected in roadway runoff from roadways and other urban land uses, although the magnitude of toxicity is highly variable. At least a portion of this variability may be due to different suspended particle size distributions, and particle concentrations, in different environments.

∞ Diverse methods for measuring roadway toxicity are available that range from enzyme activity measurements to analysis of community composition. Most toxicity studies utilize whole-organism tests (e.g. survival), as these methods combine high regulatory utility and ecological relevance with moderate cost.

∞ Use of a single toxicity test to assess roadway runoff is not recommended due to species-specific differences in sensitivity to contaminants. A battery of test species that includes a crustacean should be used. The use of toxicity identification evaluations (TIEs) is an effective tool to guide the selection of management actions in response to the presence of unacceptable levels of toxicity.

Chapter 5 Particle Size Distributions and Contaminants in Roadway Runoff

∞ A large fraction of the heavy metal and non-polar organic contaminant load in roadway runoff is adsorbed to particles. Most BMPs for roadway runoff are designed to treat only the particulate fraction. Hence, toxicity and contaminant reductions by BMPs are limited by the degree to which pollutants/toxicity associate with particles, and the efficiency with which BMPs remove particles, both of which can vary with particle size.

∞ Measurement of particle-bound pollutants in roadway runoff involves three basic steps: solid/liquid separation, solubilization of particulate bound contaminants (digestion), and analytical measurement of the solubilized contaminants. While there are numerous procedures reported in the literature, there are no regulatory approved or standardized methods for measuring particle-bound contaminants in roadway runoff. Currently employed methods are adapted from methods used for soil, solid waste, and wastewater quality analyses.

∞ The concept of contaminant bioavailability is often used for toxicity prediction. However, no relationships or methods have been established to determine bioavailability of particulate contaminants. Although controversial, methods such as sequential extraction and acid volatile sulfides, used for contaminated soils and sediments, may be possible approaches to assess heavy metal bioavailability potential of roadway runoff contaminants.

1
INTRODUCTION AND OVERVIEW

The purpose of this report is to present a state-of-the-art literature review on the co-occurrence of particles, contaminants and toxicity in roadway runoff. The specific goals of the report are to (1) document what is known about the relationship between particle size, pollutant levels, and toxicity in runoff from roadway facilities; (2) critically examine existing methods for the collection of storm water samples and subsequent measurements of toxicity, heavy metals, organic contaminants, and particle size distributions; and (3) identify knowledge gaps that limit Caltrans' ability to mitigate roadway runoff pollution through the development and implementation of BMPs.

The report is organized as follows. Chapter 1 is an overview of the relationship between particles, contaminants, and toxicity in roadway runoff. Chapter 2 reviews established and emerging methods for characterizing particle size distributions in roadway runoff. Chapter 3 reviews methodologies for fractionating particles by size for subsequent analysis. Chapter 4 reviews the relationship between particles and toxicity in roadway runoff. Chapter 5 reviews the relationship between particles and contaminants in roadway runoff. The appendix contains an annotated bibliography of relevant articles and reviewed with special emphasis on stormwater treatment implications.

1.1 CONTAMINANTS AND TOXICITY IN ROADWAY RUNOFF

Roadway and pavement runoff contains organic and inorganic contaminants that can impair receiving water quality and disrupt aquatic and benthic ecosystems [1-31]. Potential contaminants in roadway runoff include suspended solids, heavy metals, hydrocarbons, indicator bacteria and pathogens, and deicing salts. Runoff from roadways contributes as much as 50 percent of the total suspended solids, 16 percent of the total hydrocarbons, and 35 to 75 percent of the total metal pollutant inputs to impaired receiving waters [29,32]. In terms of toxicity and health risk, heavy metals, organic contaminants and microorganisms are frequently cited as the contaminants of most concern in runoff. For example, Rose *et al.* (2000)[33] found a link between storm events and increased incidence of gastrointestinal disease in the U.S., presumably due to the delivery of human pathogens to drinking water supplies by storm flows. Inputs, pathways, and receiving water impacts of contaminants in roadway runoff are illustrated in Figure 1.1. The principal sources of contaminants in roadway runoff from roadways are atmospheric deposition (precipitation and dust fall), automobiles, and the road surfaces themselves [4-8]. Contaminants can also be generated by biochemical reactions that occur within sediments [7,39,40].

The composition of particles in stormwater is illustrated in Figure 1.2, together with fractionation and measurement techniques applicable for particular ranges of particle size. Chapter 2 and 3 of this report are devoted to describing the methods (and instrumentation) available for measuring particle size distributions and fractionating particles for subsequent chemical or toxicological tests.
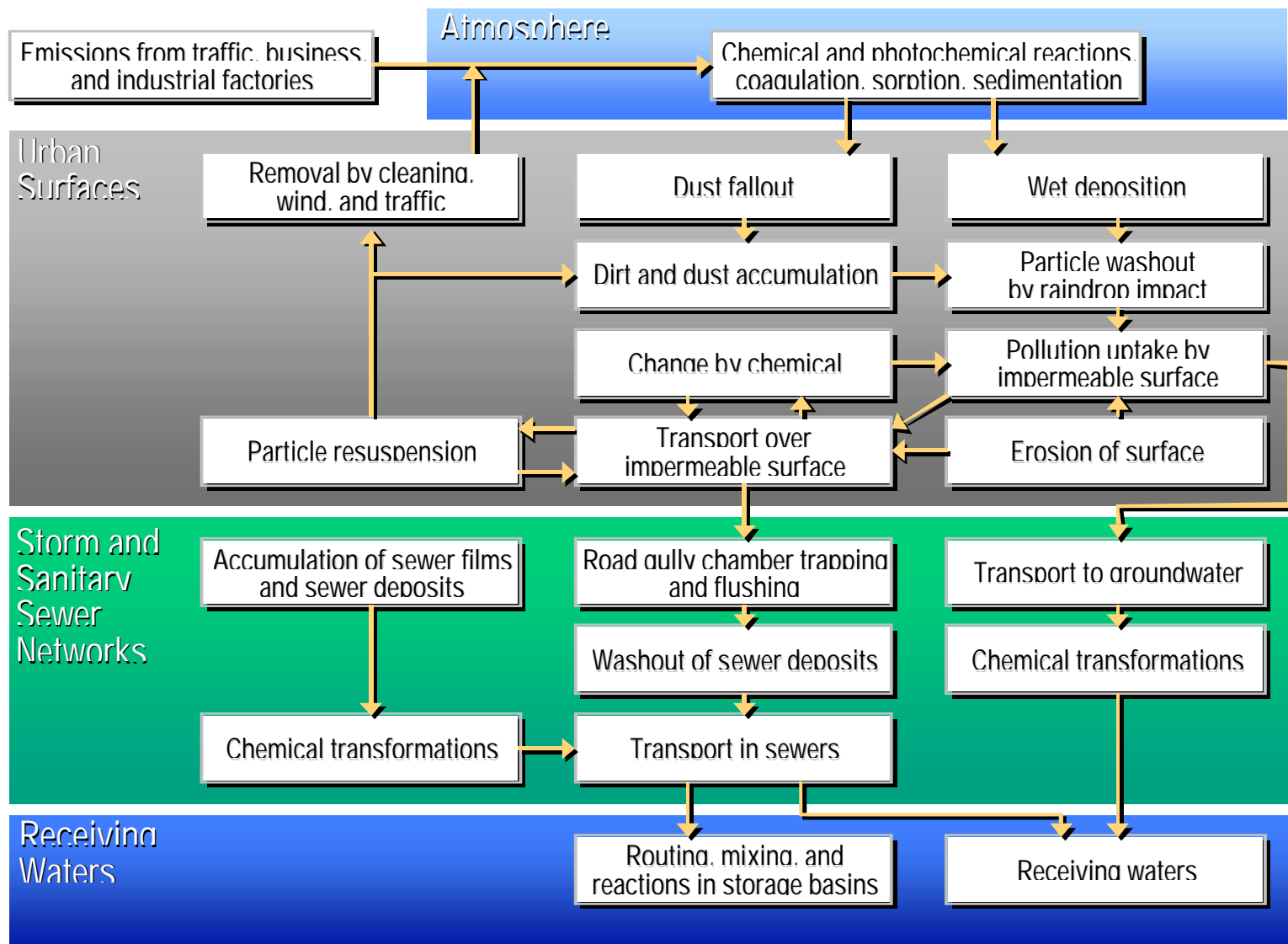
Figure 1.1 Urban runoff contaminant sources and pathways

Representative particles

Synthetic organic compounds   Algae , protozoa

Fulvic acid   Bacteria

Humic acids   Cell fragment   Bacterial flocs

Nutrient   RNA   Viruses   Organic debris

Polysaccharides   DNA   (food and human wastes)

(e.g. starch, cellulose , pectin)

Fatty acids

Protein

Separation techniques

Sedimentation

Gel filtration chromatography   Centrifugation

Bio-Gel A-1.5M

Sephadex G-1   Bio-Gel A-150M   Steric field flow fractionation

Sephadex G-25

High pressure liquid chromatography

Membrane-filter technique

Sieves

Ultra molecular sieves   Conventional suspended-solids test

Measurement techniques

Light obstruction technique

Light microscope

Scanning electron microscope

Coulter counter

Hydrodynamic chrmatography   HiAC particle counter

Laser light scattering

Centrifugal sedimentation   Gravitational Sedimentation

10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0} 10^{1} 10^{2} 10^{3} 10^{4}

Particle size (µm)

Figure 1.2 Size range of representative particles (top) , separation techniques (middle) and measurement techniques (bottom)

1.2 THE IMPORTANCE OF PARTICLES IN ROADWAY RUNOFF

Particles play a role in virtually every process illustrated in Figure 1.1 by (1) delivering the contaminants to roadway surfaces as dust and dirt [39,41-48], (2) affecting how readily the contaminants are mobilized during storms [1,8,49-52], and (3) influencing the physical, chemical and biological transformations that contaminants undergo as they are transported to receiving waters through sanitary and roadway runoff sewer systems [53-65]. In receiving waters, particles modulate the biological impact that contaminants have on aquatic and benthic organisms (i.e., pollutant toxicity) [23,66-75].

1.3 CONTAMINANT CLASSIFICATION AND TREATMENT

Particles in roadway runoff are a potential reservoir of chemical contaminants that cause toxicity [23,41,46,49,52,56,57,59,67-69,70,72,73,76-84]. Particles can also sequester human pathogens (viruses, bacteria, and protozoa) and reduce the effectiveness of disinfection strategies [85-88]. Indeed, some researchers propose using measurements of suspended particles (e.g., turbidity) as an indicator of contaminant loads [89,90]. However, extracting from the published literature general rules about the relationship between particles, contaminants and toxicity is complicated by the many different definitions of what constitutes a "particulate contaminant", the site-specific nature of the many published studies, and artifacts associated with fractionating contaminates based on particle size.

The common practice of separating contaminants into "dissolved" and "particulate" fractions using an arbitrary size-cut-off (typically 0.45 μm) reveals relatively little about the functional behavior of contaminants in engineered or natural systems. Particle-bound contaminants can pass through a 0.45 μm filter, and hence be misclassified as "dissolved" [91]. Alternatively, contaminants associated with highly porous flocs can be retained on a 0.45 μm filter, but exhibit properties such as very slow settling velocities that are typically associated with the "dissolved" fraction [42,92].

In this report we advocate a particle classification scheme based on a paper by Gustafsson and Gschwend [93] that separates contaminants into four fractions or pools-- "dissolved", "colloidal", "gravitoidal", and "sediment"--based on the expected behavior of contaminants within each fraction. Contaminants dynamically transfer between fractions by sedimentation, erosion, coagulation, fragmentation, adsorption and desorption. These dynamic phenomena should be considered and ideally exploited in BMP design (see Figure 1.3).

Dissolved Pool is defined as "any constituent that lacks an internal environment and whose fate is not affected by coagulation-breakup mechanisms nor gravitational settling."

Colloidal Pool is defined as "any constituent that provides a molecular milieu into and onto which chemicals can escape from the aqueous solution and whose environmental fate is predominantly affected by coagulation-breakup mechanisms, as opposed to removal by settling" [93].
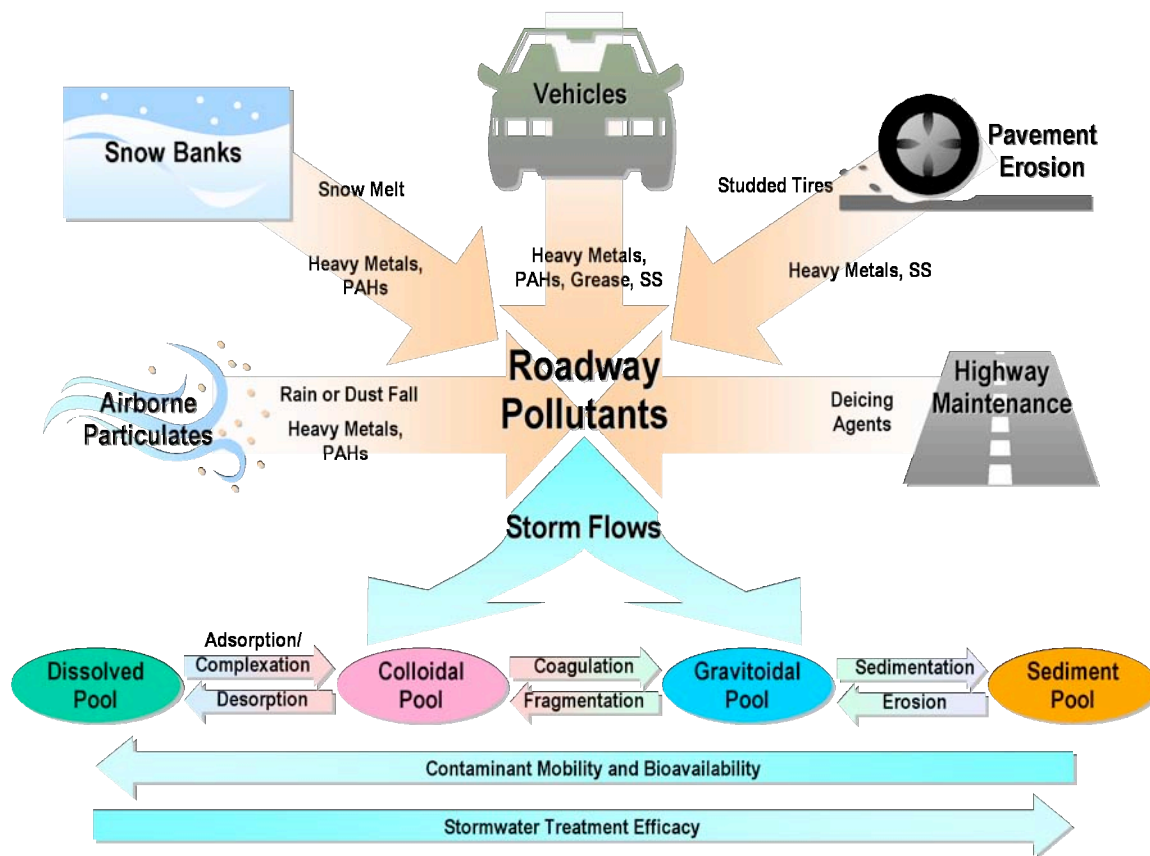
Figure 1.3
Conceptual framework for the role particles play in affecting the fate,
Transport, and environmental impact of contaminants in stormwater.

Gravitoidal Pool is defined "as any constituent that can bind chemical contaminants and rapidly settles through water by gravitational sedimentation."

Sediment Pool is defined "as all particulates associated with sediment deposited on highway surfaces, or in the storm sewer system."

These contaminant pools cannot be cleanly divided on the basis of a single set of arbitrary sizes cutoff. This is because the structural character of molecular material (e.g., globular vs. linear proteins) determines whether the molecule has an internal environment, and hence is dissolved or colloidal. Likewise, the characteristic length-scale that separates colloids from gravitoids is determined by the density and fractal structure of the aggregates [94], and by the overall solids concentration of the suspension [68]. The critical size separating colloids from gravitoids depends on the solids concentration because the latter influences the rate at which particle mass is transferred up the size spectrum by coagulation [95,96].

The degree to which contaminants in roadway runoff partition to, and co-transport with, the colloidal size fraction depends on several key physical characteristics of the particles in question,[93].:

- The surface potential of the colloid can affect the equilibrium partitioning of ionic contaminants (e.g., heavy metals) between the dissolved and colloidal pools.

- The organic content associated with a colloid can affect the equilibrium partitioning of hydrophobic contaminants [e.g. Polycyclic aromatic hydrocarbons (PAHs)] between the dissolved, colloidal, gravitoidal and sediment pools.

- The transference of colloids into gravitoids by coagulation can influence the impact of gravitational settling on the transport of contaminants.

- The internal environment of a colloid can influence the type of chemical transformations (e.g., redox reactions, photolysis, etc.) that a contaminant undergoes.

- Heavy metals like copper may first associate with organic colloidal material, and then be transferred to larger size classes by coagulation. Hence, the association between heavy metals and gravitoids may involve colloidal intermediates.

Figure 1.3 is a conceptual diagram showing how the particle classification described above applies to contaminants in roadway runoff. Once mobilized by storm flows, road surface contaminants dynamically partition between the dissolved, colloidal, gravitoidal, and sediment pools. As indicated in the figure, a central conundrum of roadway runoff BMP development is that the bioavailability, toxicity, and mobility of contaminants generally *decrease* with particle size (large bottom arrow pointing left), while the ability of BMPs to remove contaminants from water generally *increases* with particle size (large bottom arrow pointing right).

Resolving this conundrum will require focused research in several key areas, including:

- Development of methods for measuring the distribution of chemical contaminants, toxicity, and pathogens between the dissolved, colloidal, gravitoidal, and sediment pools.

- Field studies aimed at understanding how these contaminant pools evolve over time and space as contaminants are mobilized by storm flows, interact with BMPs, transport through engineered or natural watersheds, and affect receiving waters.

- Development of sampling and analytical methods for measuring the biological impact of the four contaminant pools on receiving waters and sediments.

- Utilization of continuous particle measurement as a tool to substitute analytical monitoring and to determine the performance evaluation of BMPs.

MEASUREMENT OF PARTICLE SIZE DISTRIBUTIONS IN ROADWAY RUNOFF

2.1 SUMMARY OF FINDINGS

There is considerable evidence that contaminants and toxicity in roadway runoff are associated with specific particle size ranges. This implies that the pollutant carrying capacity associated with roadway runoff, and the most effective best management practices, will be strongly influenced by the particle size distribution present in the flow. This chapter presents a review of the available technologies for measuring particle size distributions, and assesses the utility of these technologies for roadway runoff applications. The primary findings presented in this chapter are as follows:

- A large fraction of potentially toxic inorganic and organic compounds in roadway runoff is associated with particles, especially the colloidal fraction. Thus, to understand the role that particles play in pollutant transport, methods are needed to characterize the physical and chemical nature of particles, and how these properties change over the particle size spectrum. The size distribution of pollutants is also important in the design of best management practices for mitigating roadway runoff impacts on receiving waters.

- A wide variety of instruments are commercially available for particle size analyses, using one or more physical properties. Some of the physical phenomena exploited include electrical properties (such as differential resistance), transport properties in the case of sedimentation and hydrodynamic chromatography, and optical properties as represented by a wide variety of light scattering phenomena.

- Some particle size instruments detect and enumerate one particle at a time (e.g. single particle counters) while others analyze the sum of measured signals (e.g., Fraunhofer diffraction, light scattering) to obtain an ensemble average.

- Single particle counter instruments are capable of giving "absolute" concentrations in terms of the number of particles per unit volume, provided that the volume element is well defined and all particle classes can be detected. For example, light obscuration instruments are routinely used for on-line monitoring of water treatment processes [97,98].

- Ensemble average methods are generally not capable of giving "absolute" concentrations because the corresponding instruments do not yield particle concentrations on an absolute basis. They are generally faster than single particle counters since they average all of the particles present in a sample, rather than

counting each particle individually. However, the single particle counters are also less subject to statistical variations arising from registering too few particles.

- A fundamental limitation of characterizing particle size distributions in roadway runoff is that no single approach can characterize the entire range of particle sizes present. This limitation arises because: (1) no single instrument can sense more than six orders of magnitude in the range of particle sizes present in stormwater, from nanometer-sized colloidal organic material to millimeter-sized sand and silt, and (2) the physical properties of particles (e.g., density, roughness, fractal structure, etc.) are highly variable and subject to systematic biases (e.g., the physical properties of large and small particles can be different).

- Some particle sizing techniques are simple and do not require significant capital expenditure (e.g., sieving and manual microscopy), but these approaches tend to be highly labor intensive.

- Automatic or semiautomatic instrumentation is less labor intensive, but the instruments can be considerably more costly. In short, there is no perfect particle-sizing instrument. The best instrument for any particular application should be selected based on the kind of information that is desired and any practical constraints that might apply. Many instruments also require pre-calibration. As with any analytical measurement, QA/QC issues should be carefully considered.

2.2 TERMINOLOGY

Sensing particles by size is a multidisciplinary endeavor, spanning the fields of physics, chemistry and engineering. Accordingly, different terms are often used in different fields to describe the same concept. In addition, the same term may have different meanings in different fields. To reduce the potential confusion generated by the inconsistent use of terminology, we have adopted a single set of terms, which, together with their definitions, are summarized in Table 2.1.

Table 2.1
Terminology used to describe particle sizing

Term	Description
Angular velocity	Angular velocity is the amount of rotation that a spinning body undergoes per unit time.
Collimated light	Light rays that are straight, parallel, and non-converging or diverging.
Electrostatic interaction	The electrostatic force acting between two charged surfaces.
Electrophoretic mobility	Electrophoretic mobility is the migration velocity of a particle in response to a voltage drop per unit field strength; represents a measure of the surface charge (both magnitude and sign) on a particle.
Equivalent spherical diameter (ESD)	The equivalent spherical diameter is the diameter of a homogeneous sphere that would generate a detector response equivalent to the measured response.
Extinction cross section	The extinction cross section has two components – a scattering cross section and an absorption cross section. It is the amount of radiation of wavelength λ that can be absorbed or scattered by a molecule. It doesn't refer to the physical size of the molecule, just how big it effectively appears to the beam.
Friction coefficient	A measure of the drag force exerted on a particle as it moves through a fluid; depending on the context, the friction coefficient is either dimensionless, or has dimensions of Force/Velocity.
Latex dispersion	A *latex* (plural = latices or latexes) dispersion is an emulsion or sol in which each colloidal particle contains a number of macromolecules.
Moments of size distribution	Mathematical approach in noting weighted sums for generating the average size, momentum and skewness of the PSD.
Monochromatic laser	Laser light composed of a single frequency.
Monodisperse	If all particles in a colloidal system are of (nearly) the same size the system is called *monodisperse.*
Monodisperse latex particles	Particles of nearly the same size in an emulsion or sol.
Polydisperse sample	If many particle sizes occur in a colloidal system, it is called polydisperse.
Refraction	The phenomenon in which light changes its speed and direction as it passes between two transparent mediums with different refractive indices.
Refractive index	Ratio of the velocity of light in a vacuum to the velocity of light in a particular medium (dimensionless).
Sedimentation coefficient	The ratio of the mass of a particle to its friction coefficient (units of time).
Thermal convection	Thermal convection, also called Rayleigh-benard convection, is the transfer of heat through fluid motion.
Unpolarized laser beam	Light waves not having a defined direction.

2.3 PARTICLE SIZE DISTRIBUTIONS

This section reviews existing approaches for measuring particle size distributions (PSDs) in water samples, the nature of available instruments, and their relative utility for analyzing roadway runoff. The focus of this review is on instruments that provide information about the particle population present in a water sample. Instruments that provide information only about single particles (e.g., optical imaging) will not be discussed.

Relative to roadway applications, the ideal particle size analyzer would (1) output the abundance of particles in a given size bin (as characterized by some length scale), (2) cover a wide size range, (3) require little in the way of assumptions about the physical properties of the particles or the dispersion medium, and (4) have a direct and tractable relationship between particle dimension and instrument response. The ideal instrument would also be robust and field-ready, and could be used for on-line monitoring. Unfortunately, this ideal instrument does not exist. It is therefore important to understand the inherent strengths and weaknesses of each type of particle sizing instrument so that the best instrument is chosen for the purpose at hand.

Existing instruments can be grouped based on the fundamental property of the suspension being measured, and the algorithm that is used to convert the signal into an estimate of the PSD[97,98]. Physical properties that can be exploited for sizing include the particles' electrical properties (e.g., differential resistance), transport properties (e.g., sedimentation, electrophoretic mobility, and hydrodynamic chromatography) and/or light scattering properties (e.g., time-averaged or static light scattering, time or spatial fluctuations in scattering intensity in the case of dynamic light scattering, and turbidity).

The types of data generated by instrumentation exploiting these diverse phenomena include the counting and sizing of individual particles as discrete events (e.g., light obscuration, resistive pulse), the generation of continuous size distributions (e.g., sedimentation, centrifugation), and the generation of moments of the size distribution (e.g., dynamic light scattering).

Instrumentation can also be classified based on whether or not calibration is required using a standard particle system (e.g. light obscuration, resistive pulse), or is not required (e.g. sedimentation and dynamic light scattering).

Regardless of which technology is employed, sizing instruments generate complex data sets at high rates, and therefore data analysis is typically incorporated into the instrument design. Most data processing software included with commercially available instruments calculate the size distribution in terms of equivalent spherical diameters. The equivalent spherical diameter is the diameter of a homogeneous sphere that would generate a detector response equivalent to the measured response. The particles present on roadways are likely to be highly irregular in shape and physically inhomogeneous, and therefore the homogeneous-sphere approximation may have little resemblance to reality. In many cases, particle volume or particle surface area would be a more useful

representation of irregularly shaped particles. The different approaches for sensing particle sizes include:

- Electrical resistive pulse technique

- Gravitational photosedimentation

- Centrifugal photosedimentation

- Hydrodynamic chromatography

- Blockage or light obscuration techniques

- Light scattering technique- Time averaged (static)

- Light scattering technique- Time dependent (dynamic)

The above particle measurement techniques are briefly described below relative to the basic concept, strength and limitations underlying their design.

2.3.1 ELECTRICAL RESISTIVE PULSE TECHNIQUE

CONCEPT

The electrical resistive pulse technique exploits the fact that the resistance (or conductivity) of a particle suspended in an electrical field will differ from that of the suspending fluid. If a non-conducting particle suspended in a weak electrolyte (e.g., one to four percent NaCl in water) is placed in a small aperture, an increase in resistance across the orifice relative to that of the medium alone is produced. The magnitude of this increase in resistance is proportional to the particle volume. As particles pass through the aperture, the resistance is measured in terms of voltage pulses that can be counted and scaled using a multi-channel analyzer. PSDs determined by electric pulse techniques are broken into 64, 128, or 256 bins, or channels, using either linear or logarithmic scaling. Hence the PSD can be resolved into relatively fine size classes. A feature of the resistive pulse technique is that the particle size range that can be resolved is controlled by the aperture tube diameter; aperture tubes are typically available with diameters of 30, 50, 100, 120, 200, and 2000μm. If the PSD spans a large range of sizes (as typically the case for roadway samples) a single sample may need to be reanalyzed several times with different aperture sizes to obtain an estimate for the entire size distribution. The results of the analysis can be output as particle volume, area, or number fraction (normalized, integrated response), which is a function of the equivalent spherical diameter.

STRENGTHS

No other property of the particle, such as refractive index or specific gravity, is required for generation of the PSD. Because the voltage response of each particle is proportional to the volume of solid material in a particle, the resulting data are, within fairly broad limits, not affected by the shape or nature of the particle.

LIMITATIONS

The conductive carrier fluid may promote particle coagulation and therefore affect the nature of the PSD during the measurement process. The sample may have to be diluted to reduce the frequency of coincidence counts; i.e., counts due to more than one particle at a time passing through the aperture. Clogging of the smallest apertures during analysis is frequently encountered for natural samples. Instruments require calibration with monodisperse latex particles of known diameter in order to assign a particle size to each voltage threshold. The technique is best suited for laboratory use because the sample must be diluted with a weak electrolyte prior to analysis to ensure that the carrier fluid is conductive. Frequent clogging of the aperture tubes, and the labor intensive nature of the measurements, are the most frequently cited limitations associated with this technique.

COMMERCIAL INSTRUMENT

The Coulter MultiSizer is an example of a commercial instrument that utilizes the electrical resistive pulse technique. The sensing region of the Coulter MultiSizer is illustrated schematically in Figure 2.1. In this figure, the particle dispersion is forced (under pressure) to pass through the aperture (highlighted in yellow) in the direction from left to right. As it passes through the aperture, each particle displaces its own volume of electrolyte. The displaced volume is sensed as a change in the voltage across the electrodes. If the instrument has been calibrated with particles of known size, each voltage drop can be converted to an equivalent spherical diameter. After enough particles are measured , the dispersion's size distribution, and moments of the size distribution, can be computed using straightforward theory.

Figure 2.1
Schematic of Coulter Multisizer aperture.
Source:http://scooter.cyto.purdue.edu/pucl_cd/flow/vol2/6/coulter/ss000103.htm

A picture of the benchtop instrument is shown in Figure 2.2. The test sample and processing equipment is housed on the right, and the computer used to process the voltage pulses is housed in the cabinet on the left.

Figure 2.2
A picture of the benchtop Coulter Multisizer.
Source:_http://scooter.cyto.purdue.edu/pucl_cd/flow/vol2/6/coulter/ss000095.htm_

2.3.2   GRAVITATIONAL PHOTOSEDIMENTATION

CONCEPT

The settling velocity of a particle suspended in water is a function of the nature of the acceleration field (e.g., gravitational or centrifugal), namely the particle's mass and friction coefficient. Hence, given certain assumptions (described below) it is possible to convert settling velocity measurements into estimates of particle size or volume. The techniques utilizing this approach differ in the nature of the acceleration field imposed on the sample, and in the way that the settling velocities are sensed. Typically, a narrow horizontal beam of parallel light, or soft x-ray, is projected through the suspension at a known depth onto a cell containing the particle dispersion. The light or x-ray beam is moved at a programmed rate that corresponds to a particular sedimentation coefficient. Alternatively, the particle concentration at two or more depths is measured simultaneously (see the description of the LUMOSED below). The attenuation of the beam indicates the concentration of the disperse phase having a particular sedimentation coefficient defined as follows:

$$S = \frac{1}{g}\frac{dx}{dt} = \frac{m_e}{f}$$
[2-1]

where m_e is the particle effective mass, f is the friction coefficient, dx/dt is the particle settling velocity, and g is the gravitational acceleration constant (equal to 9.81 m^2/s). The sedimentation coefficient, which has units of time, is a measure of how fast the suspension settles under the influence of gravity. Particles with greater mass, or smaller friction coefficients, will settle more rapidly and hence have a larger sedimentation coefficient. For perfect spheres of diameter d suspended under laminar flow conditions in a medium with viscosity η_0, the friction coefficient can be estimated using Stokes' law as $f = 3\pi\eta_0 d$. Similar expressions for the friction coefficients are available for regularly shaped but non-spherical particles (e.g., ellipsoids) [99]. These expressions for the friction factors implicitly assume that the settling of particles is not "hindered" by particle-particle interactions. Hence, they only apply for cases where the particle concentrations are relatively low, ideally less than 0.5 percent [100]. The size range that can be measured using standard gravitational sedimentation instruments is typically from 10 to 300 μm, although the lower bound can be decreased if reasonable analysis times are allowed.

STRENGTHS

This method is relatively robust for estimating the distribution of sedimentation rates represented in a sample. Because the physics of particle sedimentation in a photosedimentation cell and a sedimentation basin are similar, the distribution of sedimentation rates obtained from the former can be directly used to design the latter[103].

LIMITATIONS

Estimating PSDs from sedimentation coefficients requires several assumptions, including information about the particles' shape (through the friction factor) and density (through the conversion between particle mass and volume). Typically, the magnitude of the friction factor and particle density is assumed to apply to all particles in the suspension, when in reality particles in roadway runoff will likely exhibit a range of friction factors and densities. The method only works if the particles in question have rapid settling rates. The latter limitation can sometimes be overcome by implementing the sedimentation measurement in a centrifuge (see next section).

COMMERCIAL INSTRUMENT

The LUMOSED is an example of a commercial instrument that utilizes gravitational photosedimentation to estimate the size distribution of particles in a fluid dispersion. One hundred fifty milliliters (150ml) of a sample is homogenized using a stirrer, and then the fluid is allowed to come to rest. The sedimentation coefficients, and PSD, for a given sample is computed by measuring the change in the solids concentration at three different levels in the sample cell with white cold light reflected by three plane mirrors (see Figure 2.3).

FEATURES OF THE LUMOSED

1. Plane mirror
2. Light source
3. Measuring levels
4. Homogenising rod (stirrer)
5. Vessel
6. Prism
7. Sensors

© Pitsch '96
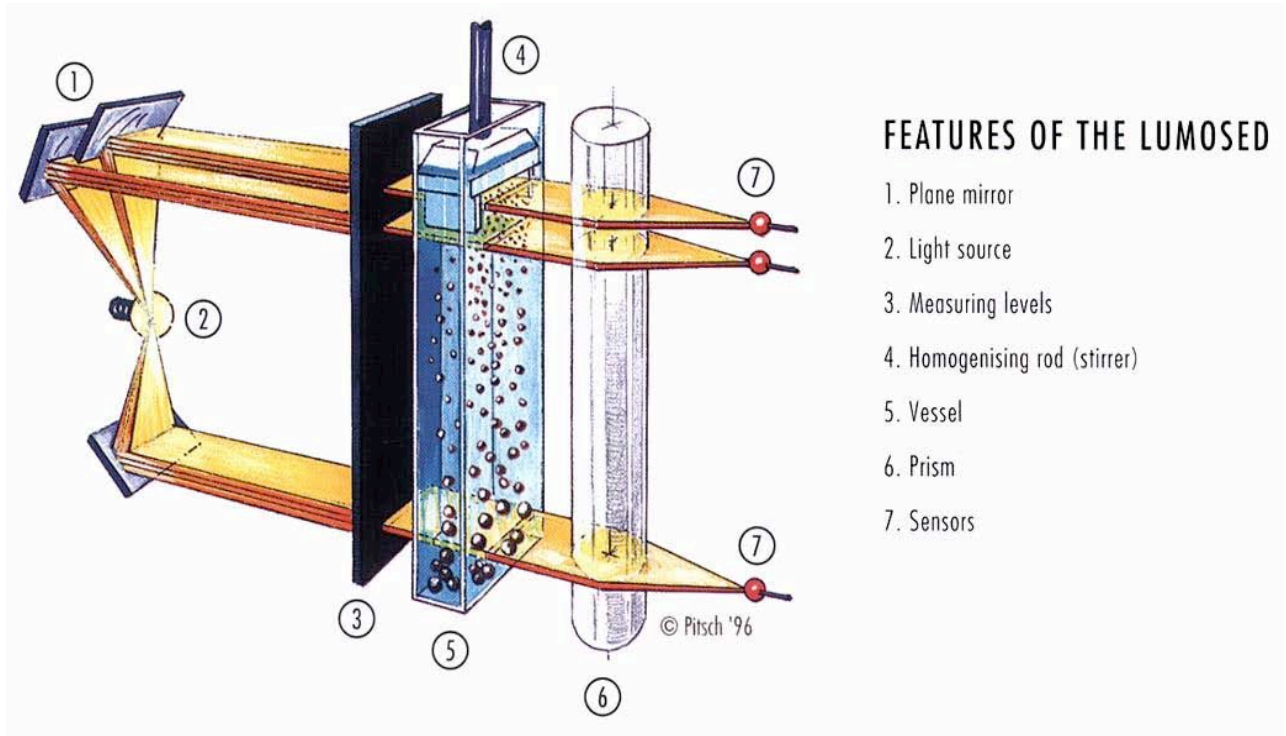
Figure 2.3
Picture of the Lumosed Photosedimentator.
Source: http://www.ejpayne.com/Lumosed.htm

2.3.3   CENTRIFUGAL PHOTOSEDIMENTATION

CONCEPT

One of the limitations of gravitational sedimentation (described above) is its inability to sense the settling rate of particles below 10 μm. This limitation can be overcome by carrying out settling experiments in a centrifuge, where the gravitational acceleration is replaced by the centrifugal acceleration. In this case the sedimentation coefficient is given by Equation 2-2, where ω is the angular velocity and r is the radial distance of the particle from the axis of rotation.

$$S = \frac{1}{\omega^2 r}\frac{dr}{dt} = \frac{m_e}{f}$$

[2-2]

Centrifugal sedimentation can be used to measure the size distribution of particles in the size range of 0.02 to 20 μm.

Instruments that utilize centrifugal sedimentation can be broken into two categories (1) homogeneous suspension method and (2) line start technique depending on the nature of the initial condition employed for the analysis, as described next.

Homogeneous (integral) suspension. In this approach, the particle suspension is uniform throughout the cell at the start of the test. The samples are centrifuged, and after some period of time, a boundary is formed that separates the particle suspension below from the supernatant on top. Because the particle velocity increases linearly with increased radial distance from the axis of rotation, it follows that the particle concentration below the boundary decreases exponentially with time of centrifugation. This is referred to as the radial dilution effect, and it is used to determine particle size by monitoring the particle concentration (or turbidity) as a function of time at a fixed depth.

Line Start Technique for Zone Transport Analysis. A density gradient is first established in the sedimentation fluid and then a thin layer of sample is added and subjected to centrifugal acceleration. Particle sedimentation occurs at velocities that depend upon size, until reaching the detector beam (light or x-ray) that passes through the fluid at a known distance below the fluid surface. The concentration of particles in the path of the detector beam is initially zero, and changes during the analysis depending upon the distribution of sizes in the sample. All particles start the sedimentation process at the same distance from the detector beam, and at the same time. Particle size is calculated from arrival time at the detector. The result of the analysis is a differential particle size distribution. Integrating the differential distribution with respect to particle size may generate an integral distribution.

STRENGTHS

Homogeneous (integral) suspension method. This approach can detect particles that are either higher or lower in density than the fluid in which they are suspended. Particles that are higher in density than the fluid settle toward the bottom of the centrifuge (that is, toward the point furthest from the center of rotation) while particles lower in density than the fluid float toward the top of the centrifuge (that is, the point closest to the center of rotation).

Line Start Technique for Zone Transport Analysis. Differential centrifugal analysis normally yields accurate and reproducible particle size distributions with very high resolution. The principal advantage of the differential method over the integral method is that many samples may be run in series without having to stop and empty the centrifuge.

LIMITATIONS

Both approaches described above suffer from rapidly changing (and difficult to characterize) conditions at the start of the analysis. Inaccuracy may also be introduced due to thermal convection of particles within the sample during analysis. These methods are also time consuming due to the overhead associated with stopping, emptying, and cleaning the centrifuge after each sample is processed. As with many of these techniques, the particle size distribution may change significantly during the centrifugation process. Hence, the resulting PSD may be an artifact of the manner in which the analysis was carried out.

COMMERCIAL INSTRUMENT

The Brookhaven Bl-DCP is a digitally controlled, high resolution, particle size distribution analyzer that uses the principle of photosedimentation in a disc centrifuge. The Bl-DCP allows the user to choose between the buffered line start and homogenous suspension methods of operation. According to the manufacturer, it yields particle sizes in the range of 0.01 to 30 μm with typical analysis times in the range from 5 to 30 minutes.

Figure 2.4
Picture of the benchtop Brookhaven BI-DCP.
Source : *http://www.bic.com/dcp.htm*

Sample

Non-porous uniform
particles

capillary

Chromatographic
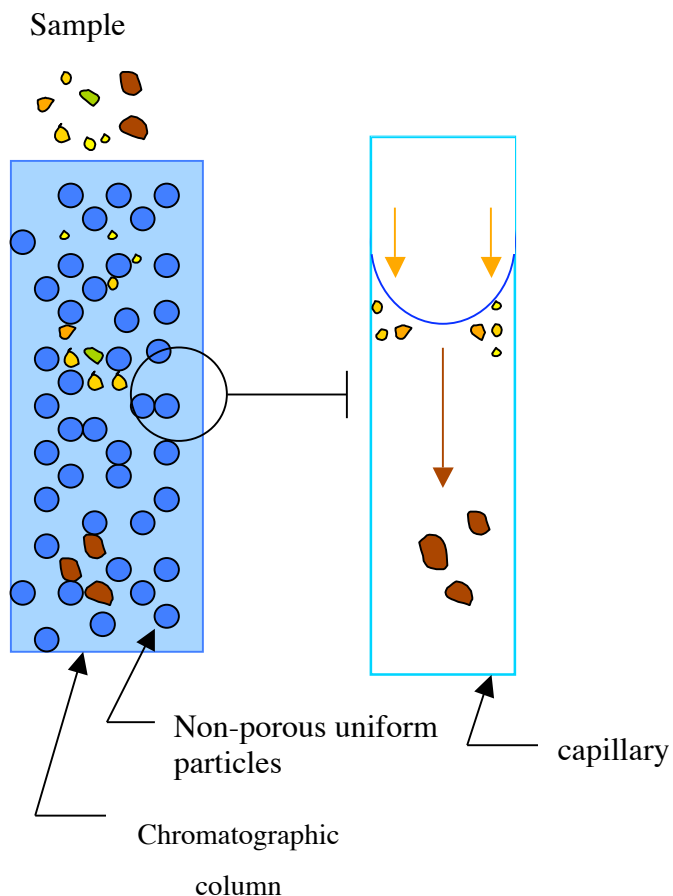
column

Figure 2.5
Basic principle of hydrodynamic
chromatography in a packed column (left)
and capillary tube (right).

2.3.4 HYDRODYNAMIC CHROMATOGRAPHY

CONCEPT

There are two methods of hydrodynamic chromatography used to measure particle size; (1) packed column chromatography (2) capillary tube hydrodynamic chromatography. Particles are injected into a liquid flowing (mobile phase) at a known flow rate either through a column packed with nonporous uniform spheres (the packed column method) or a long capillary tube (the capillary tube method).In either case, variation of flow across the interstitial voids (in the case of the packed column method) or across the capillary (capillary tube method) cause larger particles to travel faster, and smaller particles to travel slower (see Figure 2.5). A detector measures the particle concentration and determines the size distribution as the particles leave the column or tube.

STRENGTHS

This method does not require much preprocessing of the sample. The ability of this approach to determine individual particle size classes depends on the nature of the particle suspension and the packing material. Separation generally improves with increasing particle size and decreasing packing material size. The practical size range of particles which can be separated by this technique is 5 nm to 3 μm.

LIMITATIONS

The simple principle described above is confounded by particle-wall interactions. For example, electrostatic interactions between the particles and packing material can reverse the elution order, so that larger particles elute more slowly than smaller particles. Hence, interpretation of the elution data is not always straightforward, and this limitation could be particularly problematic for environmental particles where particle charge heterogeneity may affect elution times.

COMMERCIAL INSTRUMENT

The PL-PSDA is a commercial instrument that operates on the principle of packed column hydrodynamic chromatography. According to the manufacturer it measures complex particle size distributions in the range 5nm to 3μm; makes no assumptions regarding the shape of the particle size distribution; generates results that are independent of particle density; has an analysis time less than 10 minutes; automates sample analysis; and generates particle size distribution with high resolution, accuracy and precision.

Figure 2.6
Picture of the benchtop PL-PSDA.
Source: *http://www.polymerlabs.com/partsize/*

2.3.5 BLOCKAGE OR LIGHT OBSCURATION TECHNIQUES

Light obscuration, or blockage, is perhaps the most conceptually straight-forward optical approach for particle size analysis, and this method is frequently used for on-line monitoring in potable water treatment [101,102].

CONCEPT

In this approach, individual particles are forced to flow through an illuminated sensing zone, momentarily casting a shadow on a photodiode (detector). The relation between voltage output V of the photodiode and the particle cross-sectional area is given by

$$V = \frac{a_p V_0}{a}$$

[2-3]

where a_p is the particle cross-sectional area, a is the cross-sectional area of the sensor, V_0 is the voltage in the absence of a particle, and V is the recorded voltage when a particle is passing the sensing zone. The flow field in the sensing zone is turbulent (high Reynolds number) which means that an irregular particle will give a variable photodiode signal; typically, only the maximum output from the photodiode is recorded.
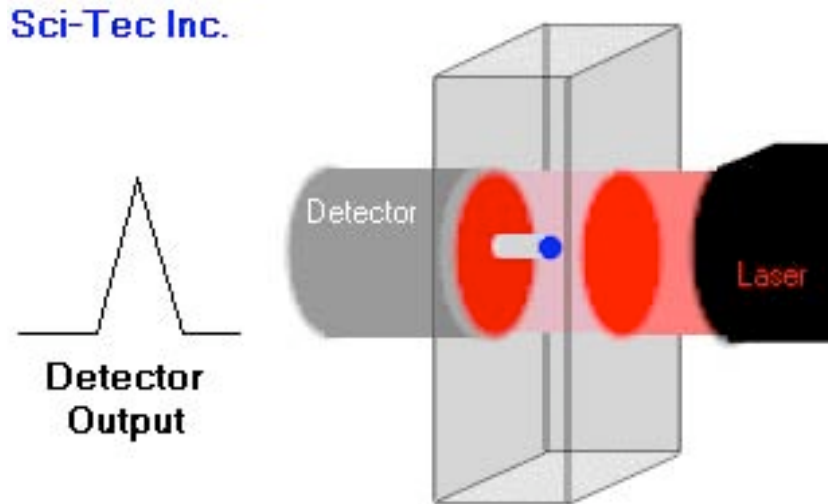
Figure 2.7
Schematic illustration of the test cell in a light obscuration instrument.
Source: http://sci-tec-inc.com/accusizert.html

As with the resistive pulse method described in Section 2.3.1, the pulse maxima are counted and sized using a multi-channel analyzer. Indeed, the optical blockage technique may be thought of as the optical analogue of the resistive pulse technique. However, a distinct advantage of the optical approach over resistive pulse method is that the carrier fluid does not have to be modified by adding an electrolyte.

When a series of sensors are employed, the particle size range that can be resolved using this technique is from about 1 μm to 1 mm, and thus this methodology extends into the sieve range. The size range for a single light obscuration sensor is typically, 1 to150 μm and 2 to 200μm, with sample flow rates between 10 mL/min and 100 mL/min [97].

STRENGTHS

Techniques involving optical principles are nonintrusive, much faster than mechanical techniques, do not require conducting media, and allow for non-disturbed sample analysis. Because of the physical nature of the response function (particle maximum cross-section), the technique would seem well suited for the analysis of extremely irregular and ill-defined particles, as compared with the response function obtained in (laser) diffraction techniques discussed below. Volume distributions are computed from the product of the particle count in each channel and the volume of a sphere having a

diameter corresponding to the geometric mean diameter assigned to that channel. Because of the variety of non-imaging optical techniques, and the number of ways in which this information can be utilized to estimate PSDs, a substantial number of instruments have been developed over the years.

LIMITATIONS

The turbulent flow field in the sensing zone can disrupt fragile flocs, and therefore this method should not be used when flocculation and coagulation efficiencies are to be quantified.

COMMERCIAL INSTRUMENT

Figure 2.8 shows the AccuSizer 780 Single Particle Optical Sizer.!Individual particles are sized by the single particle light obscuration technique.!By measuring thousands of particles, size distributions are generated.! No assumptions regarding the shape of the distribution and no complex algorithms are required to calculate results.

Figure 2.8
Picture of the benchtop AccuSizer 780
Source: http://sci-tec-inc.com/accusizert.html

2.3.6 LIGHT SCATTERING TECHNIQUE

When a beam of incident light interacts with a particle, it can be absorbed, scattered, or transmitted. Three different limits are recognized, based on the magnitude of the size parameter (p) which, in turn, depends on the index of refraction (m) of the particle relative to the suspending medium, the wavelength (λ) of the light striking the particle, and the diameter of the particle (assumed here to be a sphere):

$$p = \frac{2\pi d \ |m-1|}{\lambda} \qquad\qquad [2\text{-}4]$$

The three limits are:

p< 0.3	Rayleigh scattering
p~ 1	Lorenz-Mie theory
p>> 30	Diffraction theory

Particle sizing instruments that exploit light scattering phenomena in the three limits are described below.

2.3.6.1 LIGHT SCATTERING TECHNIQUE: DIFFRACTION INSTRUMENTS

CONCEPT

Diffraction theory applies in the case where the suspended particles are much larger than the wavelength of incident light (i.e., $p >> 30$). These instruments typically consist of a He-Ne unpolarized laser beam that is spatially filtered, expanded to about 10 mm, and collimated. Particles that migrate into the laser beam scatter light, which is focused by a lens onto the detector. The resulting pattern of scattered light (specifically, light intensity as a function of scattering angle θ) is then mathematically converted into an estimate of the PSD. Lenses of different focal lengths can be employed to focus on different portions of the particle size spectrum; typical lenses and detector combinations can resolve particle sizes in the 1 to 100 μm, 2 to 200 μm, and 6 to 600 μm range. It is even possible to extend the range to over 2 mm. Typically, the size range covered by any one lens is divided into fifteen logarithmically increasing size ranges with ratio of largest to smallest diameter of about 100:1.

STRENGTHS

Instruments employing this technique are considered easy to use and particularly attractive for their ability to analyze over a broad size range in a variety of dispersion media. Diffraction instruments do not require calibration. This is because the diffraction patterns obtained from a particular sample are converted directly into estimates of particle size.

LIMITATIONS

The resulting PSD estimates are only accurate if the instrument is properly aligned, the appropriate theory is being used to convert signal to particle size, sampling errors are negligible, and detector response is either spatially uniform or properly corrected in the software. The theory employed to convert diffraction patterns into particle sizes, Fraunhofer diffraction theory, generally breaks down for particles smaller than 10 μm. The error associated with sizing particles smaller than 10 μm can be reduced by employing a first-order correction to Fraunhofer diffraction theory or by adding a different light source with a detector at 90 degrees. These latter modifications are claimed to extend the sizing range down to 0.1 μm, but caution is always advised when evaluating manufacturer claims. Another potential problem is that the mathematical

formulations used to convert diffraction patterns to PSDs will break down if the concentration of particles is too high or too low. The ideal operating range of particle concentrations can be estimated as follows:

$$0.005 < \pi \ r^2 N_i l_p < 0.5 \qquad\qquad\qquad [2\text{-}5]$$

where r is the average particle radius, N_i is the number of particles per unit volume, and l_p is the path length along the laser beam over which particles are present during the measurement; for example, the distance between parallel windows in a sample cell.

COMMERCIAL INSTRUMENT

The CILAS 920 laser particle size analyzer is an example of an instrument that uses Fraunhofer and Mie theory to convert scattered light to PSD estimates. The sample, dispersed in liquid or gas, passes through a monochromatic laser beam. The light is diffracted by the particles, and the diffracted light is measured by a multi-channel silicon detector. The manufacturer claims that the instrument can sense particles in the range of 0.3 to 400 μm without any mechanical adjustment or optical realignment.
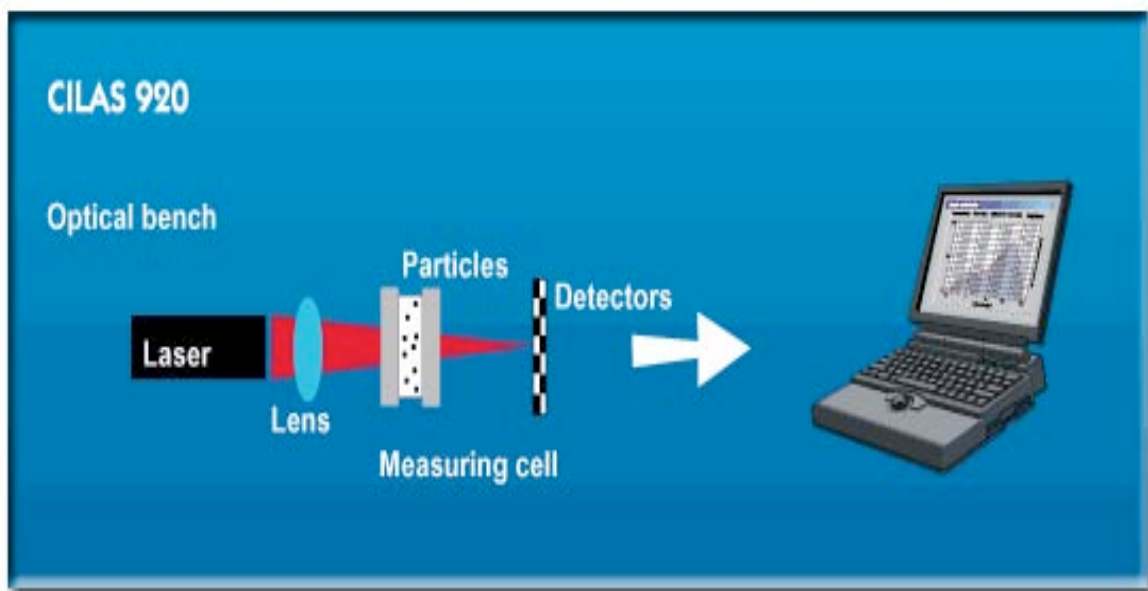
Figure 2.9
CILAS laser particle size analyzer.
Source: http://www.cilas.com/englais3/html/angranul/range/f920.htm

2.3.6.2 LIGHT SCATTERING TECHNIQUE: TIME-AVERAGED (STATIC)

CONCEPT

Smoluchowski and Einstein found that the intensity of scattered light is the result of fluctuating polarizability per unit volume. According to their theory, the polarizability per unit volume at any position and time can be divided into the sum of a constant part and a fluctuating part. The constant part gives rise to refraction and the fluctuating part gives rise to scattering. The intensity of the scattered light, according to fluctuation theory, is calculated from the mean-square fluctuations in the suspension.   For particles much smaller than the wavelength of the impinging light, (p < 0.3) the time-averaged intensity is:

$$\langle I_s(q) \rangle = KNM^2 P(\theta)B(c)$$ [2-6]

where $\langle I_s(q) \rangle$ is the time-averaged scattered intensity from the particles, q is the wave, K is an optical constant, N is the number of particles contributing to the scattering, M is the mass of the particle, P is the form-factor, θ is the scattering angle, B is the concentration factor, and c is the concentration. The wave vector q is defined as follows,

$$q = \frac{4\pi n}{\lambda_0} \sin\frac{\theta}{2}$$ [2-7]

where n is the index of refraction of the suspending medium. Since the mass of the particle is proportional to its volume, the M^2 term in Equation 2-6 gives rise to a d^6 factor in the scattering. The particle form factor $P(\theta)$ is a result of intraparticle interferences.

Formulas for P exist for simple shapes and sizes smaller than $\lambda/2$. Fortunately, in the limit of $\theta \to 0$, the particle form factor goes to unity. Furthermore, as $c \to 0$, $B(c) \to 1$. Because photon detection is a very sensitive technique, measurements can often be made in very dilute suspensions where the latter limit would apply. Alternatively, measurements can be conducted as a function of concentration with extrapolation to $c = 0$.

STRENGTHS

When the sample being analyzed contains macromolecules this method is useful for determining molecular weight, radius of gyration (a size parameter in the form factor), and second virial coefficient (a parameter in the concentration factor) from the integrated or time averaged intensity of scattered light. These features could be employed to characterize natural organic matter in road runoff; e.g., in the case where the natural organic matter in road runoff is known (or suspected) to harbor a large fraction of the contaminant of interest.

LIMITATIONS

Time-averaged intensity measurements are often plagued by the presence of very large particles in the suspension. The presence of very large particles leads to a systematic increase in scattering intensity. The only way to handle "over-sized" particles is to remove them during the sample preparation procedure.

COMMERCIAL INSTRUMENT
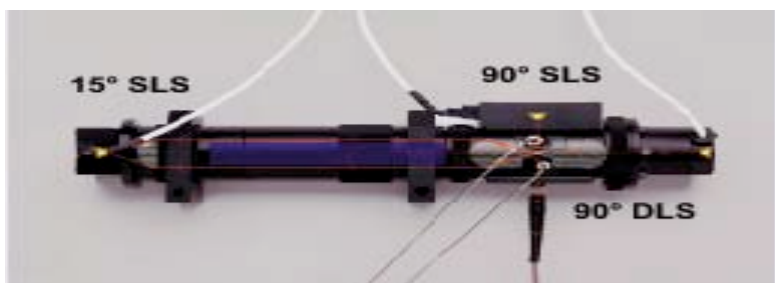
Figure 2.10
Static and Dynamic Laser Light Scattering Detector
Source: www.postnova.com

The Postnova analytics PN3000 SLS/DLS Laser Light Scattering Detector series is a new type of modular detection system, which combines different physical light scattering principles at the same time. The system enables the simultaneous and independent measurement of static laser light scattering at an 15 ° and an 90 ° angle as well as the measurement of dynamic laser light scattering at an 90 ° angle. The detection takes place in an extremely small and sensitive light scattering cell with a total volume of only 10 μL. Due to that possible multidimensional detection the sample can be investigated simultaneously from various viewpoints. In this way complex polymer and particle systems, where the use of only one detection technology is not sufficient, can be characterized.

2.3.6.3 LIGHT SCATTERING TECHNIQUE: TIME-DEPENDENT (DYNAMIC)

CONCEPT

In a liquid suspension of small particles, molecules of the liquid strike the suspended particles, causing them to move randomly around some average value. These particles are said to be in Brownian motion. When light of uniform wavelength generated from a light source strikes particles in Brownian motion, a Doppler shift occurs, changing the wavelength of the light. The magnitude of this shift in wavelength is related to the size of the particles. Smaller particles move faster than larger particles and scatter light at a

higher frequency.!By measuring and analyzing the scattered light over time (dynamic light scattering), the particle size distribution of the suspended particles can be determined. The intensity of scattered light is proportional to the square of their electric field, and it too is fluctuating in time. The statistics of these fluctuations can be characterized by an autocorrelation function defined as follows.

$$c(\tau) = \langle I(0)I(\tau) \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T I(t)I(t-\tau)dt \qquad \text{[2-8]}$$

where the intensity I has, in general, different values at time t and $t-\tau$.. T represents the duration of the total experiment over which the product of the intensity with delayed version of itself is averaged.

STRENGTHS

The dynamic light scattering system delivers high-precision measurement from nano to micron range. Experiments involving monodisperse polystyrene latex particles indicate that the technique gives results comparable to those obtained from electron microscope [104]. Additional information on the theory of time-dependent, or dynamic, light scattering can be found in Berne and Pecora (1976)[105].

LIMITATIONS

The equivalent sphere diameter d, here called the hydrodynamic diameter, may be larger than the diameter of a particle measured by electron microscopy, due to the fact that a layer of solvent molecules may be included in the hydrodynamic diameter. For polydisperse samples, the interpretation of dynamic light scattering data is difficult. Since the technique does not involve counting of single particles, size distribution information must be obtained from the deconvolution of the sum over all single exponentials contributing to the measured autocorrelation function. Several numerical techniques have been utilized for this purpose, including direct inversion [106], Laplace transformation [107], and the method of cumulants [108]. Detailed deductions based on the results of the deconvolution can be very misleading, especially for broad distributions. Dust, or over-size particles, can seriously compromise the deconvolution step, and lead to erroneous size distribution curves, artificially large estimates for average particle size and polydispersity. For this reason dynamic light scattering would not be a good choice for characterizing the PSDs in roadway samples.

COMMERCIAL INSTRUMENT

The Horiba LB-500 uses dynamic light scattering technique for estimating particle size distributions. The optical system of the LB-500 is as shown in Figure 2.11. The light emitted by the semiconductor laser is straightened by the lens into parallel rays, which are focused by the lens to pass through the hole in the mirror, and again by a lens to pass through the pinhole. The light passing through the pinhole is then once again made parallel by the lens and directed at the cell unit. The gathered light is aimed at the particles in the cell. The light scattered from the particles is received by the entire lens, passed through the pinhole, and then returned to the mirror with the hole along the same

path. This light is finally reflected by the mirror and gathered into the detector by the lens. This instrument is purported to measure particles in the size range of 3nm to 6 μm
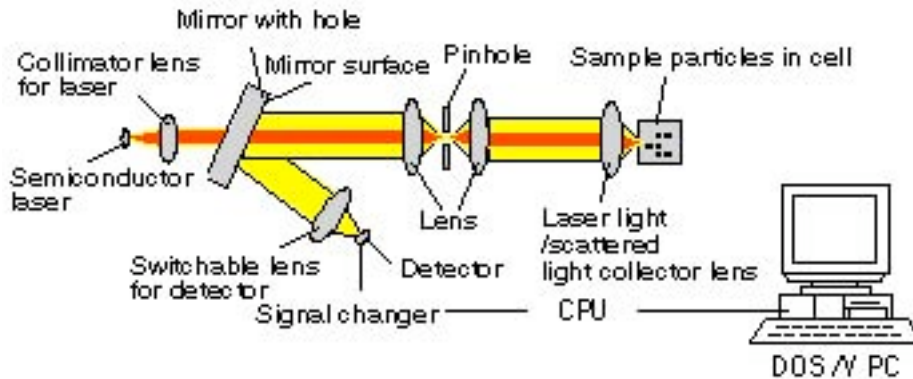
Figure 2.11
Optical system of the HORIBA LB-500
Source: *http://global.horiba.com/analy_e/lb-500/lb-500_10.htm*

2.4 COMPARATIVE EVALUATION OF THE COMMERCIALLY AVAILABLE PARTICLE SIZE MEASUREMENT INSTRUMENTS

Tables 2.2 and 2.3 summarize the commercially available particle sizing instruments (Table 2.2) and the strengths and limitations of each particle sizing methodology (Table 2.3). The list of manufactures and instrument names presented in Table 2.2 is not exhaustive, but includes all particle sizing instruments for which information was found on the word wide web.

Table 2.2
A summary of commercially available particle sizing instrument and the methodology employed

Technique used	Manufacturer	Instrument name	Size range	Time required
Electrical Resistive pulse technique	1. Confocal lab	Coulter Multisizer II	0.4 – 1200 μm	NA
	2. Coulter Corporation (USA)	Coulter Multisizer II	0.4 – 1200 μm	NA
	3. Beckman Coulter	Coulter Multisizer 3	0.4 – 1200 μm	NA
	4. Coulter Electroniks GmbH	Coulter Multisizer II	NA	NA
	5. Micromeritics Instrument Corporation	Elzone	0.4 – 1200 μm	10 -100 sec
Gravitational Photosedimentation	1. E.J Payne Ltd.	Lumosed Photosedimentometer	0.5 – 250 μm	3 min.
	2. Micromeritics Instrument Corporation	Sedigraph 5100	0.1 – 300 μm	NA
	3. Chemical Process specialists	CPS GS 100	5 – 500 μm	NA
	4. FRITSCH GmbH	Analysette 20 Sedimentograph	0.5 – 500 μm	3 – 10 min
Centrifugal Photosedimentation	1. Broohaven Instrument Corporation	BI-DCP	0.01 – 30 μm	5-30 min.
	2. Horiba Instruments Inc.	CAPA 700	0.01 – 300 μm	NA
	3. Shimadzu Scientific Instrument	SA-CP4	0.01 – 500 μm	NA
Hydrodynamic chromatography	1. Polymer Laboratories	PL-PSDA	5nm - 100 μm	<10 min.
	2. Matec Instruments Companies Inc. (Matec Applied Sciences)	CHDF 2000	0.010 – 3 μm	<10 min.
Light obscuration technique	1. Sci-Tec Inc.	Accusizer 780	0.5 – 5000 μm	5 min.
	2. Particle Sizing systems	Accusizer 780	0.5 – 2500 μm	NA

Table 2.2 Continued

Technique used	Manufacturer	Instrument name	Size range	Time required
Light Diffraction	1. CILAS	CILAS laser particle size analyser	0.3 – 400 µm	~ 30 sec (liquid mode)
				~15 sec (dry mode)
	2. Horiba Instruments Inc.	LA-920	0.02 –2000 µm	20sec
		LA-300	0.1 – 600 µm	~ 20 sec
	3. FRITSCH GmbH	Analysette 22 (Comfort)	0.8 – 1250 µm	10 sec
		Analysette 22 (Economy)	0.1 – 600 µm	10 sec
		Analysette 22 (Compact)	0.3 – 300 µm	10 sec
	4. Sympatec GmbH	HELOS	0.1 – 8750 µm	NA
	5. Microtrac Inc. A Unit of Nikkiso Co., LTD.	SRA 150	0.7 – 700 µm	NA
	6. Shimadzu Scientific Instrument	SALD -3001	0.1 – 2000 µm	NA
Dynamic Light Scattering	1. Horiba Instruments Inc.	LB-500	3nm - 6 nm	2 min.
	2. Sci-Tec Inc.	The Nicomp 380	1 – 5000 nm	5 min.

NA=Not Available

Table 2.3
Strengths and limitations of the different particle sizing methodologies.

Comparison Parameter	Electrical resistive pulse technique	Gravitational photosedimentation	Centrifugal photosedimentation	Hydrodynamic chromatography	Light obscuration technique	Diffraction instruments
Assumption regarding shape or nature of particles	No	All particles are assumed to have the same shape and density	All particles are assumed to have the same shape and density	No	Well suited for analysis of extremely irregular particles	No
Calibration required?	Yes	No	No	Yes	Yes	No
Artifacts generated during analysis	PSD may change during analysis (e.g. by breakage of aggregates)	PSD may change during analysis	1) The centrifugal force may affect the original PSD. 2) Thermal convection of particles within the sample during analysis	Electrostatic interaction between particles and packing material may complicate data interpretation	Turbulent flow field in the sensing zone can disrupt fragile flocs.	Resulting PSD estimates are only accurate if the instrument is properly aligned, the appropriate theory is being used, sampling errors are negligible
Modifications made to the original sample	Sample is diluted using weak electrolyte	No	Density gradient is established in the line start technique.	No	No	No
Limitations on the particle concentration in the sample	No	Particle concentration should be less than 0.5%	No	No	No	Cannot give accurate results if particle concentration is too high or too low.

3
PARTICLE FRACTIONATION

3.1 SUMMARY OF FINDINGS

To better characterize the relationship between particles and contaminants, methods are needed to separate particles by size for further analysis. This chapter discusses several methods for fractionating particles by size and their potential utility for the analysis of roadway runoff. The primary findings presented in this chapter are as follows.

- Typically, pollutants are classified as either "dissolved" or "particulate" based on whether or not they pass through a 0.45 µm filter. The 0.45 µm division between dissolved and particulate phases has a long history in the field of water quality. However, the choice of a single cut-off is arbitrary when applied to samples of roadway runoff, because the particle size distributions extend continuously from tens of nanometers (e.g. hydrated metal ions) to hundreds of micrometers (e.g. suspended matter).

- There are several different approaches available for fractionating particles by size. Particles with length scales in excess of approximately 100 µm can be fractionated using conventional wet or dry sieving, typically with nylon sieves. Sequential filtration, thin-cell split flow fractionation, and elutriation can be used to fractionate particles in the size range of 1 to 100 µm. Gel permeation chromatography (GPC) in defined gel phases and sequential ultrafiltration (UF) can be used to fractionate the colloids smaller than 1 µm into classes based on size, mass, or electrical properties, to name a few.

- Chemical toxicology and physical characterization of a single particle size fraction typically requires about 1 gram of material. This constraint means that samples must undergo a significant concentration step prior to fractionation. For example; if 50 to 100 grams of solids are required for complete physical and chemical characterization of the fractionated sample, then approximately 50 to 10,000 L of roadway runoff must be analyzed.

3.2 TERMINOLOGY

Terminology used in this chapter to describe particle fractionation are summarized in Table 3.1

Table 3.1.
Summary of particle fractionation Terminology

Term	Description
Aperture	Size of holes in a sieve
Concentration polarization	Accumulation of rejected solute on the feed side of the membrane or filter surface, excluding cake or adsorbed layers. Interrupting or stopping the filtration process allows the concentration polarization to dissipate
Hydrated metal ions	All metal ions are hydrated in aqueous solution. Hydrated metal ions become acids in water.
Hydrometer	A device used to measure the densities of liquids and solutions
kDa	Kilo Daltons. A unit of molecular weight
Mesh	Number of wires (or openings) per inch of square
Polydispersity	The state of non uniformity in molecular weight

A summary of the many different techniques available for fractionating particle by size and their target size range is presented in Fig 3.1.
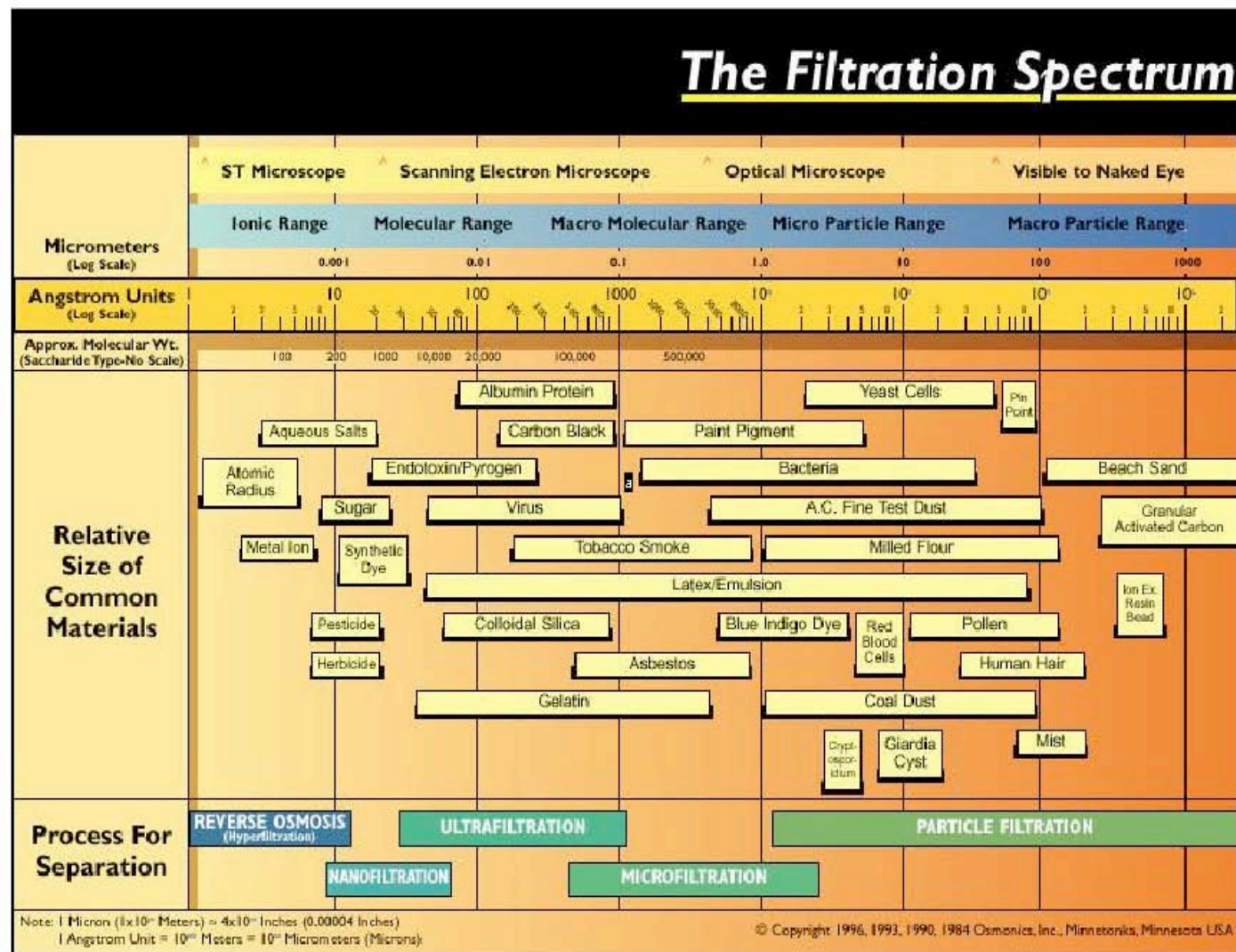
Figure 3.1 Filtration Spectrum
(Courtesy of GE Osmonics, Inc.)

3.3 LARGE PARTICLE FRACTIONATION

Particle fractionation techniques that might find application in roadway runoff studies include wet or dry sieving, sequential filtration (SF), split-flow thin cell separation (SPLITT), and reverse flow elutriation (RFE). Each of these methods, and their inherent strengths and limitations, are discussed below.

3.3.1 WET/DRY SIEVING

CONCEPT

Sieving consists of passing a sample through a series of sieves of known mesh size, having progressively smaller pore openings, and collecting and quantifying the material caught on each sieve. Particles smaller than the smallest pore size (usually about 63 μm) can be quantified as one fraction, or can be further separated – when suspended in water - by time-limited sedimentation. The quantity of material in each fraction can be evaluated by drying and weighing, or by measurement of concentration through specific gravity determination with a hydrometer or by measurement of the volume displaced when the solids in that fraction are added to water. Runoff studies and the different types and sizes of sieves used are summarized in Table 3.2.

Figure 3.2
Perforated Wire and perforated
Plate Sieves from Endecotts Ltd.

Table 3.2
Types and Sizes of Sieves Used in Stormwater Studies

Study	Sieve type	Sieve sizes used, microns
Ran et al. (2000)[109][a]	Nylon sieves Wet sieving	25
Colandini et al. (1995)[110]	Dry sieving Nylon sieves	2000, 1000, 500, 250, 125, 80, 63, 40
Prytula and Pavlostathis (1996)[111][b]	Wet sieving Stainless steel sieves	0.25 in., 1,400, 106, 53
Sansalone and Buchberger (1997)[52]	Dry sieving	9500, 4750, 2000, 850, 425, 250, 150, 75, 63, 45, 38, 25
Legret and Pagatto (1999)[14]	Dry sieving Nylon sieves	2000, 500
Krein and Schorer (2000) [46]	Wet sieving	630, 200, 63

[a] used to study the fractionation and particulate materials in rivers
[b] used to study the fractionation and particulate materials in a contaminated estuarine sediment

Sieving can be carried out either wet or dry. In wet screening, material is washed evenly over the screen to prevent clogging. Also small particles are washed off the surface of the large ones. The mesh and size of sieves are standardized in most countries (see listings of Standard Test methods, including ASTM and ISO methods in the Appendix to this report). Sieving can be used to fractionate particles ranging in size from approximately 44 microns (American mesh size: 325) to 4 mm (American mesh size: 5). Fine sieve cloth is usually woven with phosphor bronze wire, medium with brass wire, and coarse with mild steel wire. Special purpose sieves are also available in stainless steel, nylon, and silk. Different sieve materials can be used depending on subsequent chemical characterization of the fractionated sample and the potential for interaction between the sample and the sieve. There is a range of commercial sieve shakers available for medium (0.2 to 4 mm) and fine (less than 0.2 mm) particles and these usually classify the particles into five or six fractions in each pass. Approximately 50 to 100g of solid material is required for sieving.

STRENGTHS

Sieving is probably the easiest and least expensive way of fractionating particles in a liquid sample [100]. Sieving is independent of the physical or chemical properties of the particles.

LIMITATIONS

A number of variables can influence sieving results, including particle shape, presence of very fine particles, initial sieve loading, time and method of agitation, cohesiveness of the powder (in dry sieving only). For example, elliptical particles would eventually pass through the sieve opening size of the smallest diameter of the particle. Computation of volumes based on this dimension would report sizes that are smaller than would be reported by methods that consider all of the dimensions of the particles. As the aperture decreases in size, the time required to sieve an equivalent mass of sample increases. If the screen contains a large proportion of material just a little larger than the aperture size, the capacity of the sieve may be exceeded. Repeatability can be high, although reproducibility is often poor due to the many variables that provide sources for user error.

COMMERCIAL INSTRUMENT

There are many different types of Sieve Shakers commercially available. One example of digital Sieve Shaker is shown in Figure 3.2. The Octagon Digital Sieve Shaker is compact and sufficiently lightweight to be portable.

Figure 3.3
Octagon 2000 digital sieve shaker from Endecotts Ltd.

3.3.2 ELUTRIATION

CONCEPT

Elutriation is a process of fractionation by means of an upward current of fluid (Figure 3.3). In a sense it is the reverse of gravitational sedimentation. Fractionation is carried out in a series of cylindrical vessels of successively increasing diameter. Thus, the fluid velocity decreases with each stage. The coarsest particles are retained in the first stage, and finer particles are retained in the following vessels . The evolving particle size distribution can be monitored during fractionation using a variety of different instruments.

From a theoretical perspective, this approach separates particles on the basis of their settling velocities. Specifically, particles with settling velocities greater than the upward flow velocity in a particular vessel will be retained, while particles with settling velocities slower than the upward flow velocity will be washed into the next vessel.The fractionation efficiency can be estimated from theoretical considerations by assuming laminar flow in the cylindrical vessels [112]. The fraction f of ascending particles in the cylinder is related to the settling velocity of the particle v_p as follows:

$$f = \frac{r_c^2}{R^2} = 1 - \frac{v_p}{v_{max}}$$

[3-1]

where r_c represents the critical radial distance at or below which a particle of settling rate v_p will be washed out, R is the radius of the cylinder and v_{max} is the maximum fluid velocity in the cylinder.

This equation assumes that particles are homogeneously distributed across the cylinder's cross-section. Clearly, if all particles have a settling velocity greater than the maximum fluid velocity, $v_p > v_{max}$, then all particles entering the cylinder will be retained. From Stokes' Law v_p is proportional to particle diameter squared, and the elutriation efficiency
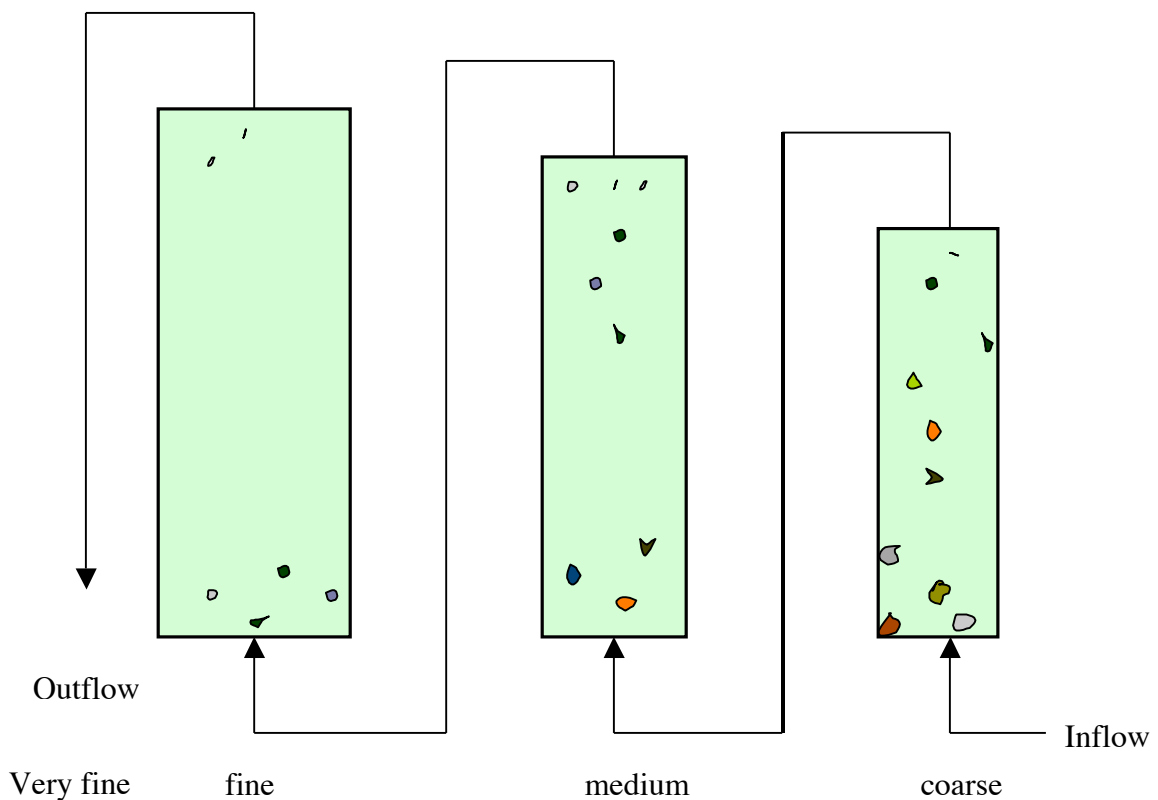
Figure 3.4
General approach for fractionating suspended particles by elutriation. The size of the retained particles decreases with increasing cylinder diameter.

can be therefore expressed as a function of particle size:

$$f = 1 - \frac{1}{2}\left(\frac{d}{\overline{d}}\right)^2$$

[3-2]

where d is the diameter of the particle being fractionated and $\bar{d}$ is the diameter of a particle whose settling velocity is equal to the average water velocity in the cylinder. From the last equation, the fraction of particles of a particular diameter that will washout, or *elutriate*, from a given cylinder can be calculated. For example, 87.7 percent of particles with a diameter that is one half of the reference particle, $d = \bar{d}/2$, will elutriate to the next larger cylinder. Fifty to Hundred grams of solid material can be fractionated in 36 to 48 hours using this approach. Although the process is time consuming, it is very low maintenance and subject to few artifacts.

STRENGTHS

Fifty to Hundred grams of solid material can be fractionated in 36 to 48 hours using this approach. Elutriation process is very low maintenance and subject to few artifacts.

LIMITATIONS

The principal disadvantage of Elutriation process is that this process is very time consuming.

3.3.3 FIELD-FLOW FRACTIONATION (FFF)

Field-flow fractionation (FFF) is the generic term for a class of techniques where particles are separated by mass, size, or other properties based on the combination of flow and some additional external field [113]. With respect to roadway runoff applications, the small load capacity of FFF is a serious limitation because adequate amounts of materials in the various particle size fractions cannot be obtained for subsequent chemical analysis. Consequently, this method will not be discussed further.

3.3.4 SPLIT-FLOW THIN (SPLITT) CELL FRACTIONATION

CONCEPT

Continuous fractionation of particles into two size classes can be accomplished utilizing fractionation across the thin dimension of split-flow thin (SPLITT) separation cell. SPLITT channels are ribbon like, unpacked, thin (usually <0.5 mm) flow channels with splitters at the outlet or at both inlet and outlet (Fig. 3.5). The sample is suspended in a carrier fluid and continuously introduced through the top inlet at a volumetric flow rate of Q_s. Simultaneously, pure carrier fluid is introduced through the bottom inlet at a flow rate of Q_c. Flow splitters near the inlet and outlet establish a stream-plane separating the two inlet streams, the position of which is dictated by Q_c and Q_s.
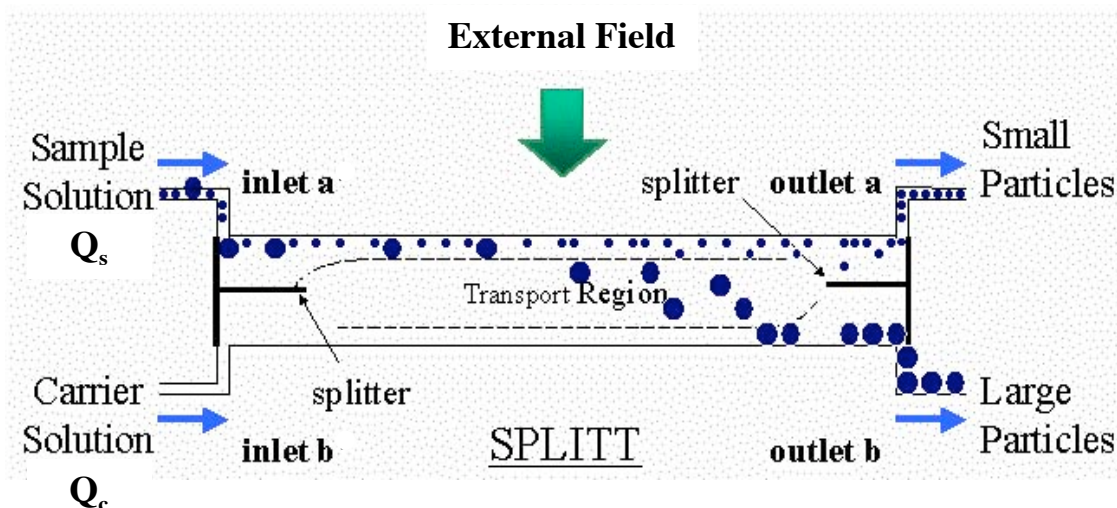
Figure 3.5
General approach for fractionating suspended particles by SPLITT.

Normally, the inlet flows are adjusted so that Q_c is considerably greater than Q_s so that the incoming particle stream is confined to a narrow lamina in the upper portion of the thin cell. As particles enter the sample zone, interaction with the gravitational field causes them to migrate vertically toward the lower cell wall. The faster settling particles emerge from the lower outlet while the remaining particles emerge through the upper outlet. A driving force or gradient is applied across the separation channel perpendicular to the flow axis to send sample components selectively into various lateral positions for separation. Force fields that can be used to induce separation include gravitational acceleration, centrifugal acceleration, electrical forces [114,115] hydrodynamic lift forces [116] and concentration gradients [117]. The separation is achieved in a few seconds to a few minutes yielding two-size fraction of the sample. Particles that are smaller than a certain cutoff diameter are collected from the top outlet (outlet a) while larger particles are collected from the bottom (outlet b). For multiple size fractionation the sample is run through the system several times using different flowrates.

STRENGTHS

SPLITT produces high-resolution fractionation with little overlap because of the uniformity of flow in the cell [118]. With SPLITT fractionation, particles are exposed to low mechanical stress and a large volume of sample can be processed rapidly. The simple structure of the system allows easy disassembly for cleaning out accumulated debris in the cell after repeated use. Also the flow within the cell is hydrodynamically very stable, leading to a high-resolution separation. The SPLITT system is a relatively new separation method capable of separating environmental particles that are within the size range of approximately 150 μm. By adjusting the flowrates coming in and out of the cell, the system can be set up to separate sample particles at a specific cutoff diameter.

Relative to environmental applications, it is possible to connect individual cells in parallel or series. In this way, the total sample flow rate can be increased and the samples can be fractionated into multiple size classes.

LIMITATIONS

Despite the theoretical elegance of the SPLITT cell method for particle separation, the instruments must be constructed with precision to obtain uniform parallel flow in the cell. While this method usually results in a clean separation of the two fractions, cross-contamination of the two fractions can occur in several ways. A small fraction of particles below the critical diameter may leak across the transport lamina and enter the wrong outlet fraction. Particles smaller than the critical diameter may enter the outlet along the edges of the SPLITT cell where the flow of transport lamina is reduced over a short distance due to frictional drag at the edge walls. A well-designed SPLITT cell can minimize cross contamination [118].

The basic SPLITT arrangement described here, based on sedimentation, is sometimes compared with elutriation. The major difference between the two systems is the non-uniform velocity profile that develops in the elutriation cylinder, which tends to blur the cutoff between particle classes.

COMMERCIAL INSTRUMENT
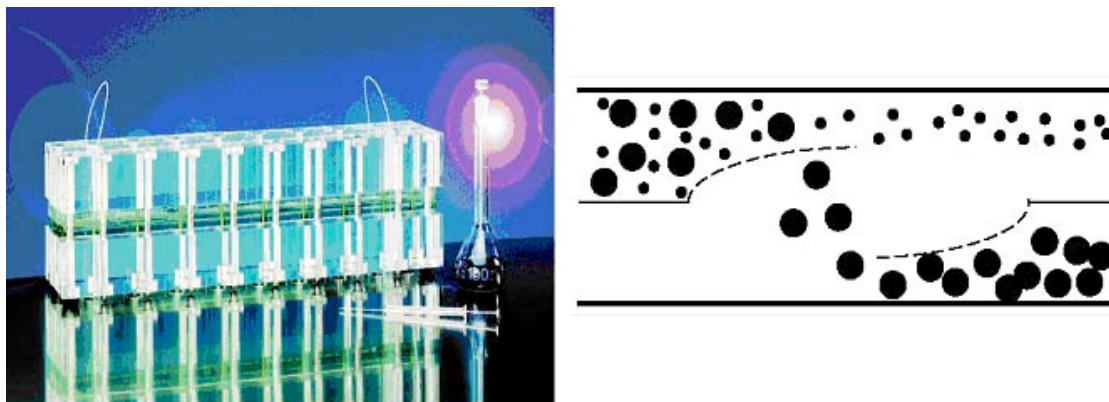
Figure 3.6
Gravitational SPLITT (left) and Side view of a typical SPLITT channel (right).
Source: www.postnova.com

SPLITT fractionation is a relatively new class of separation method. It can be used to separate a diverse range of samples such as environmental (sediment, colloids), pharmaceutical/ biotech (cell organelles, bioparticles , starch granules) and other samples as diamond particles, carbon black , silica etc. with a size from $50\mu m$ down to about $1\mu m$ (for laboratory use only).

SPLITT fractionation utilizes the well-controlled hydrodynamics found in thin cells and simplicity and flexibility of an externally applied field. The high stability of flow leads to

high resolution separations and reproducible results. Since a known field is applied, the separation is predictable and can be fine-tuned for individual samples. The field, typically gravitational in nature, is oriented in a direction perpendicular to the laminar flow of the carrier fluid through the cell. When the field is provided by the Earth's gravity, the overall cell design is a simple flow channel.

3.4 SMALL PARTICLE AND MACROMOLECULE FRACTIONATION

Due to the extreme complexity of colloidal and macromolecular material in environmental samples, and the absence of species specific separation procedures, only a rough fractionation of materials in the micron and submicron size range can be achieved. In practice, fractionation can be achieved based on: (1) different properties of the macromolecules, for example their varying hydrophilic/hydrophobic interaction with sorbents in high-performance liquid chromatography (HPLC) systems [119,120], (2) different affinity to metal-containing sorbents, (3) different behavior in electric fields (e.g. conventional and capillary electrophoresis, size-exclusion in gel chromatography), and (4) size discrimination on ultrafiltration membranes of adequate molecular mass cut-off. Among the separation principles mentioned above, the fractionation of dissolved submicron colloidal and macromolecular materials by ultrafiltration (UF) on suitable membrane filters is a simple way to separate polydisperse mixtures as a function of their molecular size. The ultrafiltration membrane fractionation is further described below.

3.4.1 MEMBRANE FILTRATION

CONCEPT

Membrane filtration is similar to sieving except that the pore sizes of membrane filters are several orders of magnitude smaller than sieves. A single membrane filtration can be used to separate particulate and soluble fractions, or a series of membrane filters with different pore sized can be used to separate particulates into different size fractions. Membrane filters work well for particles in the 0.01 to 1 μm size range. In water treatment, membrane filters in this size range are referred to as microfilters. Membrane filters with smaller pore sizes can also be used. However, these types of filters, typically referred to as ultrafilters, separate solids based on their molecular weight rather than physical size. Based on this literature review, only one study (Characklis and Wiesner, 1997)[56] was identified as having used membrane filters (microfilters) to separate runoff particulates into different size ranges (0.45μm, 0.1μm, and 0.01μm). Ran et al., 2000 [109] used a commercial tangential flow filtration system (Millipore-Pellicon Model ON 133) to separate three fractions in the colloidal (<1μm) size range in rivers (1 to 0.2μm, 0.2 to 0.006μm, and 0.006 to 0.003 μm).

STRENGTHS

A wide range of membrane and filtration devices are commercially available. Furthermore , the methodologies employed are well developed and documented .

LIMITATIONS

Filters can clog quickly, causing the effective pore size to drop dramatically. When this happens, colloids that initially passed through the filters begin to be retained. For substances that occur substantially in the colloidal size fraction (e.g., Fe, Pb), this can lead to significant errors in assigning the metals to "dissolved" or "particulate" fractions, as is often done based on filtration data. Fortunately, overloaded filters quickly reveal themselves by declining filtration rates and increasing back-pressure. Another disadvantage associated with the membrane approach is that the size distribution of particles within a given fraction cannot be determined without introducing significant experimental artifacts [94]. The increase in local particle concentration that occurs at the surface of the membrane can accelerate the coagulation and flocculation of particles. On the other hand, removing particles from the membrane by vigorous stirring, and the adding of dispersants, can lead to the break-up of flocks that were present in the initial sample. In any case, the size distribution of particles captured on a membrane will probably bear little resemblance to the size distribution of the same material in the undisturbed sample.

COMMERCIAL INSTTRUMENT

Figure 3.7
Pelicon Tangential Flow Filtration device from Millipore Corporation

The Pellicon 2 cassette system is a tangential flow filtration (TFF) device for use in the laboratory, pilot plant or small-volume production facility. The systems use Pellicon 2 cassette filters, which according to the manufacturer are available in a range of ultrafiltration and microporous membranes.

PARTICLES AND TOXICITY IN ROADWAY RUNOFF

4.1 SUMMARY OF FINDINGS

Roadway runoff may disrupt natural ecosystems by contributing toxicity. The role that particles play in this process is an emerging field, complicated by a diversity of environmental settings and analytical techniques. This chapter reviews the methods used to measure toxicity from roadway runoff, their adaptability to assessing the role that particles play in delivering toxicity from roadway runoff and the state of knowledge that currently exists on this topic. The primary findings of this chapter are as follows.

- Particles influence chemical toxicity by contributing stress to test organisms, altering bioavailability, and modifying exposure level. Sampling and toxicity test methods used in most roadway runoff monitoring programs are not adequate to assess biological impacts related to particles in roadway runoff.

- Toxicity is frequently detected in roadway runoff from roadways and other urban land uses, although the magnitude of toxicity is highly variable. At least a portion of this variability may be due to different suspended particle size distributions, and particle concentrations, in different environments.

- Diverse methods for measuring roadway toxicity are available that range from enzyme activity measurements to analysis of community composition. Most toxicity studies utilize whole-organism tests (e.g. survival), as these methods combine high regulatory utility and ecological relevance with moderate cost.

- Use of a single toxicity test to assess roadway runoff is not recommended due to species-specific differences in sensitivity to contaminants. A battery of test species that includes a crustacean should be used.   The use of toxicity identification evaluations (TIEs) is an effective tool to guide the selection of management actions in response to the presence of unacceptable levels of toxicity.

4.2 TERMINOLOGY

Toxicity assessment of stormwater and roadway runoff is a relatively new field that is characterized by the use of a diversity of methods, and variable terminology. Terms frequently used to describe roadway runoff and roadway runoff toxicity are defined in Table 4.1.

Table 4.1
Terminology used in evaluating the effects of contaminants on aquatic test organisms (after Tchobanoglous, Burton, and Stensel [120])

Term	Description
Acute toxicity	Exposure that will result in significant response shortly after exposure (typically a response is observed within 48 or 96 h)
Chronic toxicity	Exposure that will result in sublethal response over a long term, often 1/10 of the life span or more
Chronic value (ChV)	Geometric mean of the NOEC and LOEC from partial and full cycle tests and early-life-stages tests
Cumulative toxicity	Effects on an organism caused by successive exposures
Dose	Amount of a constituent that enters the test organism
Effective concentration (EC)	Constituent concentration estimated to cause a specified effect in a specified time period (e.g., 96 h EC_{50}).
Exposure time	Time period during which a test organism is exposed to a test constituent
Inhibiting concentration (IC)	Constituent concentration estimated to cause a specified percentage inhibition or impairment in a qualitative function
In vitro (in glass or test tube)	Tests conducted in glass petri dishes or test tubes
In vivo (in living organism)	Tests conducted using the whole organism
Lethal concentration (LC)	Constituent concentration estimated to produce death in a specified number of test organisms in a specified time period (e.g., 96-h LC_{50})
Lowest-observed-effect concentration (LOEC)	Lowest constituent concentration in which the measured values are statistically different from the control.
Maximum-allowable-toxicant concentration (MATC)	Constituent concentration that may be present in a receiving water without causing significant harm to productivity or other uses
Median tolerance limit (TL_m)	An older term used to denote the constituent concentration at which at least 50 percent of the test organisms survive for a specified period of time. Use of the term "median tolerance limit" has been superseded by the terms median lethal concentration (LC_{50}) and median effective concentration (EC_{50})
No-observed-effect concentration (NOEC)	Highest constituent concentration at which the measured effects are no different from the control
Sublethal toxicity	Exposure that will damage organism, but not cause death
Toxicity identification evaluation (TIE)	A laboratory approach for identifying the constituents of an environmental sample that are responsible for measured toxicity

4.3 INFLUENCE OF PARTICLES ON RUNOFF TOXICITY

Suspended particles in roadway runoff have the potential to affect biological communities in three ways: direct physical impacts, altered bioavailability of bound contaminants, and as a source of contaminant exposure in benthic or sediment-ingesting organisms.

Physical Effects of Particles. High concentrations of suspended particles can produce adverse effects by damaging and interfering with fish gills or other delicate structures, and through the ingestion of non-nutritive material by filter-feeding organisms.

Particle Effects on Bioavailability. The bioavailability of both metal and organic contaminants is influenced by a contaminant's affinity for particle surfaces. Laboratory studies have shown that a wide variety of particle types can reduce the bioavailability of toxins such as chlordane [68].

Particles as a Source of Exposure. Experiments with filter-feeding and sediment-ingesting organisms demonstrate that contaminants bound to particles are bioavailable through dietary assimilation [69,73,74]. Because runoff particles contain higher concentrations of contaminants (on a mass basis) than do bed sediments [72,121], these particles may represent a significant source of chronic toxicant exposure.

Contaminants are mostly reversibly bound to suspended runoff particles, thus these particles may represent a source of water column toxicity or interstitial water toxicity. The short-term release of particle-bound contaminants to the water column does not appear to have a significant effect on the toxicity of roadway runoff samples. Based on Toxicity Identification Evaluation (TIE) studies, (see description later) it has been found that removal of the particulate fraction has little effect on the magnitude of runoff toxicity [122,123]. Desorption of contaminants over time periods of hours to days may be a significant factor affecting the toxicity of sediment interstitial water, however. Laboratory elutriation studies showed that roadway runoff particles released toxic quantities of unidentified materials into clean seawater in less than 24 hours [72].

4.4 FACTORS INFLUENCING RUNOFF TOXICITY

In addition to suspended particles, there are multiple factors that can influence contaminant bioavailability, or the sensitivity of an organism to runoff toxicants (Table 4.2). Ultraviolet light exposure has been shown to influence the toxicity resulting from roadway runoff exposure *in situ* [124]. Exposure to ultraviolet light can affect the toxicity of photoactive compounds, including several PAHs, through two mechanisms: photomodification and photoinduction. Photomodification occurs when certain PAHs (e.g., phenanthrene, naphthalene, pyrene, and anthracene) are converted to more toxic byproducts in the water column [125]. These compounds can also react with ultraviolet (UV) light after bioaccumulation to produce highly toxic intermediates [126]. Both of these processes have been shown to occur at environmentally realistic exposure levels. Ireland et al. [124] demonstrated that a portion of the *in situ* toxicity of runoff to *C. dubia* is due to UV exposure, implicating the action of PAHs in runoff toxicity. UV light activation is not usually incorporated into laboratory toxicity tests, so the toxicity of PAHs in runoff water may be underestimated.

Table 4.2
Factors influencing roadway runoff toxicity

Factor	Effect	Toxicants Affected
Suspended solids	Reduces bioavailabity of water column toxicants	Metals and organics
Temperature	Alters metabolic rate of organism, thermal stress may enhance toxicity	General effect
Salinity	Altered solubility, speciation, and uptake	Metals
Sediment oxidation state	Controls binding/solubility of metals, metals may be more bioavailable in toxic sediments	Metals
Sediment organic carbon	Binds toxicants and reduces bioavailability	Metals and organics
Background contamination	Pre exposure of resident organisms may induce detoxification systems and increase tolerance to toxicants	Metals and organics
Ultraviolet light exposure	Alters chemical structure and enhances toxicity in water and tissues	PAHs

4.5 TOXICITY IN STORMWATER RUNOFF

The lack of standardized study designs for assessing toxicity in roadway runoff prevents synthesis of published data for the purpose of discerning national trends or associations with land use [127]. As shown in Table 4.3, both acute and chronic toxicity has been detected using a variety of test species, in both roadway runoff and base flows. Toxicity monitoring of runoff samples in the San Francisco Bay area detected toxicity in over 90 percent of the samples, regardless of land use [4]. Toxicity was also detected in up to 40 percent of runoff samples from a variety of land uses in other parts of the United States [16,23]. Tests of agricultural and urban runoff in California using the water flea *Ceriodaphnia dubia* have detected toxicity in numerous counties [128]. Over 90 percent of runoff samples (dry and wet weather) from Ballona Creek, draining a highly urbanized watershed near Santa Monica Bay, were toxic to marine species [66,122].

The severity of runoff toxicity is highly variable, however. The threshold of toxicity (highest concentration with no observed effect, NOEC) has been reported to range from less than 6 percent to 50 percent in samples from the same location [66]. The magnitude of toxicity detected also depends upon the test method used. In some cases, the toxicity of a single sample of roadway runoff can vary by a factor of 4, from nontoxic to *C. dubia* to a NOEC of 25 percent to *Strongylocentrotus purpuratus* [27]. Factors contributing to this variability include the use of different test methods among the studies and variations in land use. There is little evidence for regional differences in roadway runoff toxicity.

Table 4.3
Comparative response of different aquatic test organisms to roadway runoff samples

Sample Type[a]	Relative Sensitivity of Test Methods[b]	Reference
Wastewater (I, M)	Water flea(S)=Microtox (L)	Doherty *et al*. [129]
Urban runoff (W,D)	Amphipod (S)>Amphipod (G)>Fish (S)	Hatch and Burton [130]
Glycol deicers (L)	Water flea (S)=Fish (S)	Pillard [131]
Urban runoff (W)	Fish (S)>water flea (S)	Lopes and Fossum [123]
Urban runoff (W)	Water flea (S)>Fish (S)	Kinnetic Laboratories, Inc.
Urban runoff (W)	Water flea>Fish=Algae	BASMAA [4]
Airport runoff (W)	Water flea=Fish	Fisher *et al*. [10]
Roadway runoff pond interstitial water	Water flea>Microtox	Dutka *et al*. [121]
Urban Runoff (W)	Sea urchin (F)>Water Flea (S)>Mysid (S)	SCCWRP [27]
Urban runoff (D)	Sea urchin (F) = Abalone (D) >Kelp (G)	Bay *et al*. [66]
Roadway runoff sediment (aliphatic fraction)	Microtox (L)>Amphipod (S)	Boxall and Maltby [132]
Roadway runoff sediment (PAH fraction)	Amphipod (S)>Microtox (L)	Boxall and Maltby [132]

[a]Sample Type Abbreviations: I=industrial waste water, M=municipal waste water, D=dry weather runoff, W=wet weather runoff, L=laboratory prepared sample
[b]Test Method Abbreviations: S=survival, L=luminescence, F=fertilization, D= development, G=growth

4.6 TOXICITY IN SEDIMENTS

Numerous studies report that roadway runoff can increase the toxicity of sediments in freshwater receiving areas. Elevated concentrations of metals (Cd, Pb, Zn, Cu) and PAHs have been detected in the sediments of streams (downstream of roadway runoff discharges) or runoff treatment ponds [70,71]. Macroinvertebrates living in these areas often contain elevated tissue burdens of metals and PAHs [5,70].

Sediment toxicity has been studied relatively little, but has been detected on several occasions in both marine and freshwater systems. Reduced amphipod survival was measured in laboratory tests of freshwater sediments collected from urban drainages or motorways [18,123]. In other studies of roadway runoff-influenced sediments, toxicity to the same species has not been detected [69].

In the coastal marine environment, reduced amphipod survival has been detected consistently offshore of an urban roadway runoff discharge in San Diego Bay ; toxicity at this site is seasonal and appears to correspond to roadway runoff discharge events (present immediately after the winter season, but not in the fall). Interstitial water

collected from sediments at the mouth of Ballona Creek (Santa Monica Bay) is occasionally toxic [72], but the effect was spatially limited as no evidence of toxicity was found in sediments further offshore of Ballona Creek [122].

4.7 TOXICITY IN ROADWAY RUNOFF

The incidence of runoff toxicity related to roadways is variable. Few studies have examined transportation land uses directly, and those that have, may be influenced by site-specific variations in water quality or test methods. Toxicity was detected in over 90 percent of roadway runoff samples from transportation-related land uses in the San Francisco area [4]. Toxicity in these samples was usually sub-lethal (reduced reproduction), whereas samples from other land uses were often acutely toxic (mortality). Hence, the causative agents of toxicity in roadway runoff may differ from those in other types of urban runoff.

Few studies have been carried out where the runoff was predominantly or exclusively from roadways. One multi-year toxicity study was conducted in Santa Clara Valley, California in which most samples were predominantly collected from freeway runoff. These samples showed high incidences of toxicity to *C. dubia*, but the toxic response was quantitatively different from that seen in samples derived from other land use categories [4]. The cause of toxicity for roadway runoff in BASMAA study was found to be non-polar organics and metallo-organics. Two other toxicity studies conducted by Pitt et al., [23] and Marsalek et al. [16] on roadway runoff reached to similar conclusions where they measured higher level of toxicity in roadway runoff compared to the other land uses. The high level of toxicity on this runoff was perhaps partially due to the presence of deicing chemicals.

Recently, Caltrans initiated a comprehensive toxicity test of runoff from their various facilities, including 24 roadway sites throughout the state (Caltrans 2003). The goal of this Statewide Toxicity Testing Research Project was to assess the toxicity associated with discharges from its storm drain system, determine the cause of the toxicity, and provide some understanding of the sources of these discharges. Depending on rainfall, three samples (first flush storm, a midwinter storm, and a storm at the end of the rainy season) were obtained from each site, and tested for toxicity. Roadway runoff was captured by grab samples in cubitainers and shipped to the Aquatic Toxicology Laboratory at the University of California, Davis. Standard EPA three-species chronic toxicity tests were carried out on the samples in accordance with established procedures. Two endpoints are reported for the *Pimephales* (fish) test: biomass and mortality. Laboratory QA/QC procedures were followed for all tests. Chronic tests were used, as they can provide significant information on acute toxicity as well. In instances where significant mortality occurred in either the 7-day *Ceriodaphnia* (water flea) or 7-day *Pimephales* chronic toxicity tests, Toxicity Identification Evaluations (TIEs) were conducted in an attempt to determine the putative cause of the toxicity. The results obtained for the past two monitoring seasons (2000-01 and 2001-02) are summarized below.

Pimephales – Of the 98 tests performed, 82 (83.7 percent) indicated toxicity for either one or both tests. Reductions in biomass were found in 52 samples, and mortality was found in 28 samples indicating that most often, reductions in biomass were common and acute toxicity was less common. No pattern in toxicity with respect to date of sampling is apparent as toxicity was found at all dates from October to May.

Ceriodaphnia – Of the 98 tests performed, 72 (73.5 percent) indicated significant toxicity. These results include all tests for which acute toxicity occurred and chronic tests were not possible to perform. As with the *Pimephales* toxicity test results, there appears to be no pattern with respect to date of sampling as significant toxicity was found throughout the entire period of sampling.

Selenastrum – Of the 98 tests performed, 46 (46.9 percent) indicated toxicity. The *Selenastrum* test was never the sole positive test result for any site at any sample date. Again, no pattern in the positive results was evident.

Toxicity Identification Evaluations – Thirty TIEs were performed on samples for which acute toxicity was observed. The TIEs indicated that no single source of toxicity was common among sites. However, nonpolar organic compounds were suggested as the putative source of toxicity in five of the TIEs, metals were suggested as the putative source in 11 TIEs, and surfactants were suggested as the putative cause in seven cases. In one case, a metabolically active pesticide was implicated, and the remainder had no discernable cause.

The Caltrans results were consistent across years with the samples collected during the 2001-02 exhibiting a slightly higher percentage of toxic samples. In general, the results from the *Pimephales* tests were almost identical in the overall percentage, and the *Ceriodaphnia* tests during 2001-02 produced a slightly higher percentage of tests with toxicity. The greatest difference is in the results of the *Selenastrum* tests performed in both years. Only a small number of samples were determined to be toxic by the *Selanastrum* test during 2000-01, but almost half of the tests resulted in toxicity during 2001-02.

4.8 TOXICITY IN RECEIVING WATERS

Toxicity has been detected in stream samples collected following storm events, establishing the potential for impacts on freshwater communities. Fewer studies have been conducted in the marine environment, because of logistical difficulties in obtaining samples from roadway runoff discharge plumes. Toxicity to marine species has been detected in surface water samples collected from the discharge plume offshore of two urban rivers in southern California [27,122]. Toxicity at these sites was proportional to the concentration of roadway runoff present; hence toxicity measurements of in-stream roadway runoff samples may provide a measure of roadway runoff toxicity in coastal waters, provided that the tests are conducted with marine species. Toxicity measurements of discrete surface water samples has been combined with more spatially extensive data on plume dispersion to describe the spatial extent of surface water toxicity due to roadway runoff discharges in marine areas. The toxic portion of the roadway

runoff plume was calculated to occupy more than one square kilometer during some discharge events, as shown in Figure 4.1 [122,133].

Altered community structures of freshwater macroinvertebrates have been observed in areas receiving roadway runoff discharge. These effects are usually expressed as reduced species diversity and the replacement of sensitive species with forms thought to be pollution tolerant [30,71,75]. Increased sediment concentrations of contaminants in roadway runoff discharge areas are often accompanied by changes in organic loading and grain size, which can complicate the interpretation of the community data. For this reason, Davis and George [5] concluded that analysis of tissue contaminant concentrations provided a more useful measure of receiving water impacts from roadway runoff discharge. Maltby *et al.* [71] used statistical analysis and a thorough characterization of habitat variables to differentiate between habitat and contaminant related impacts on macroinvertebrate assemblages from roadway runoff.

In situ exposure experiments have also shown that roadway runoff discharges are capable of producing toxicity to resident organisms. Reduced survival of freshwater crustaceans (amphipods or water fleas) placed in cages has been observed at stream locations downstream of roadway runoff discharges [20,30,130]. The causes of *in situ* toxicity are difficult to determine in many cases, because the animals are exposed to high variations in stream flow, turbidity, dissolved oxygen, and ammonia, in addition to elevated contaminants. Statistical analysis [20] or exposure manipulations [124] have been used in some studies to show that mortality was likely due to trace metals or PAH exposure.
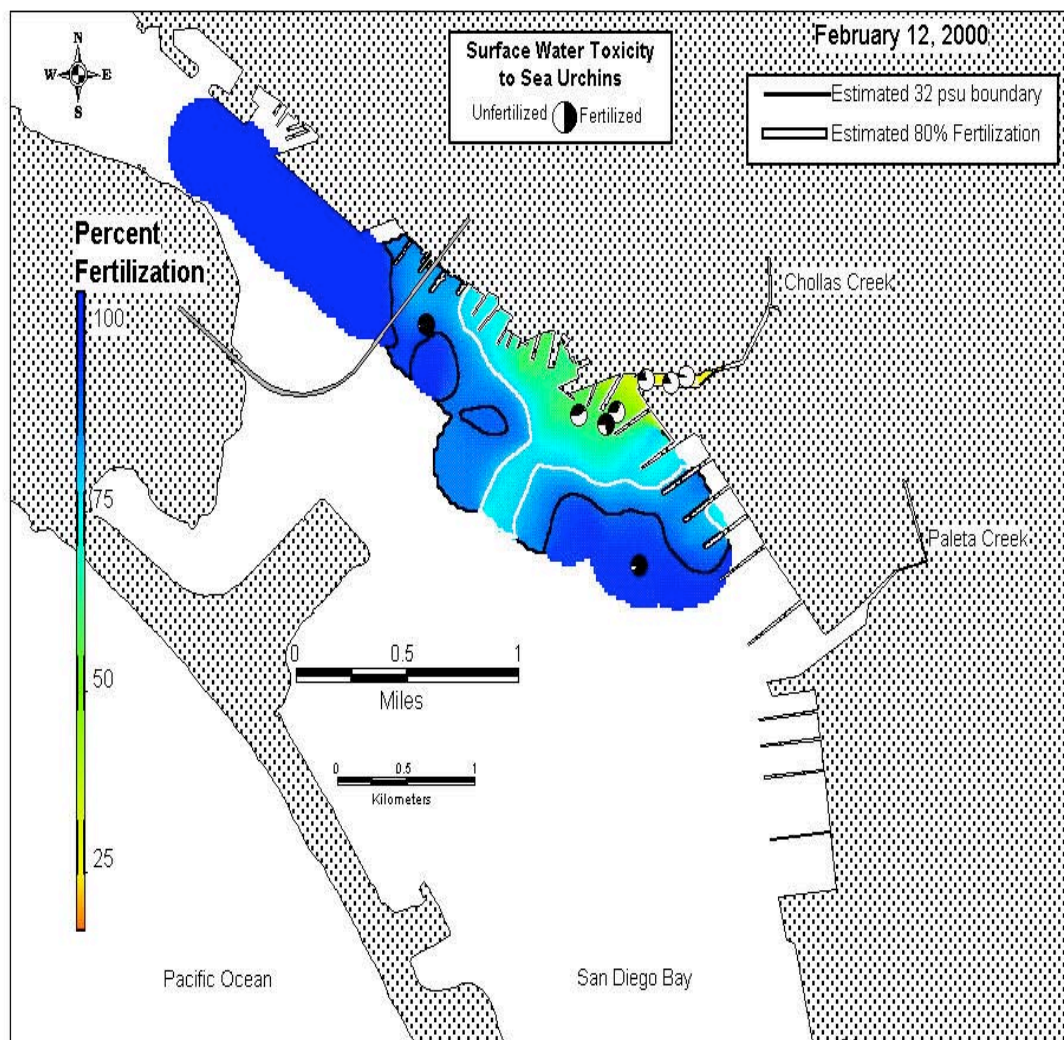
Figure 4.1
Chollas Creek surface plume toxicity map (from Schiff et al. [109]). The colors show the calculated percent of sea urchin fertilization based upon the toxicity results for water samples (indicated by pie diagrams) and measured salinity in the surface layer.

4.9 TOXICITY MEASUREMENT

None of the existing biological test methods were developed expressly for the purpose of evaluating runoff from roadways or other urban land uses. Instead, studies are conducted using a variety of laboratory toxicity test methods or field survey methods originally developed for other applications.

Hundreds of different biological test methods are available for measuring the toxicity of environmental samples, including roadway runoff. These methods can be categorized by the type of response measured. There are four primary categories of response, which

correspond to increasingly complex levels of biological organization as summarized in Table 4.4.

Table 4.4
Potential test systems for assessment of roadway runoff toxicity

Response Category	Example
Biochemical	Metabolic enzyme activity
	Mixed function oxidase enzyme (P450) induction
	Cholinesterase activity
	Stress protein induction
	Vitellogenin induction
Physiological	Respiration rate
	Bioluminescence
	Scope for growth
Whole Organism	Mortality
	Growth/development
	Reproduction
	Bioaccumulation
	Feeding rate
	Preference/avoidance
Population and Community	Abundance
	Diversity
	Colonization
	Multimetric index (e.g., IBI)

Biochemical response tests measure biochemical changes in a test organism, including measurement of enzyme activity and protein production. Biochemical responses may occur within minutes of contaminant exposure, may be contaminant specific, and can often be detected with a high level of sensitivity.

Physiological response tests measure the combined activities of multiple enzyme systems and thus integrate biochemical changes occurring throughout the organism. The physiological and biochemical responses measured in toxicity tests represent naturally occurring processes in the organism, so these responses may be strongly influenced by environmental factors such as temperature, feeding, and reproductive state.

Whole organism response tests integrate the biochemical and physiological effects of toxicants and are expressed as changes in survival, growth, reproduction, or behavior of the organism. The majority of laboratory toxicity tests measure effects at the whole organism level.

Population and community response tests identify changes in abundance and composition of multiple species that constitutes a community of organisms. Responses at

this level are commonly measured as changes in the abundance of species, diversity, or as an index of response based on the combination of several different attributes.

Each test category outlined above has positive and negative attributes relative to their sensitivity, cost, and ecological relevance (Table 4.5). Biochemical and physiological test methods are often very sensitive and relatively inexpensive to conduct, but it is often difficult to determine a threshold of response that has adverse impacts on the health of the organism.

Table 4.5
Characteristics of biological test systems (after Buckler and Granato [127])

Response Category	Relative cost	Relative sensitivity	Chemical sensitivity	Ecological relevance	Regulatory utility
Biochemical/physiological	Low	High	High	Low	Low
Whole organism	Medium	Medium	Medium	Medium	High
Population/community	High	Low	Low	High	Medium

Community level responses have the greatest ecological relevance, as they represent the effects of long-term exposure and are usually based upon changes actually occurring at the location of interest. It is difficult to ascribe changes at the community level to contaminant effects, however, because similar changes are produced by natural events, such as changes in habitat type, physical disturbance, or temperature.

Most biological assessment programs use whole organism tests in order to minimize the disadvantages associated with other types of tests. Measurements of mortality, reduced growth, or inhibited reproduction are relatively inexpensive to perform, sensitive to contaminant exposure, and have a straightforward association with community-level responses.

4.9.1 TOXICITY MEASUREMENT IN ROADWAY RUNOFF

Roadway runoff toxicity is most frequently measured using one of the methods developed for the assessment of Whole Effluent Toxicity (WET). WET methods are used for National Pollutant Discharge Elimination system (NPDES) compliance monitoring and are conducted using standardized protocols developed by the U.S. EPA for freshwater [134] or marine environments [135]. Three freshwater species are used most commonly for testing: a crustacean known as the water flea (*Ceriodaphnia dubia*), a fish (*Pimephales promelas*), and a single-celled alga (*Selenastrum capricornutum*).

Marine species are less commonly tested, although much of California's urban runoff is ultimately discharged into coastal waters. The most commonly used marine species for assessing roadway runoff toxicity are the sea urchin (*Strongylocentrotus purpuratus*) and the mysid (*Americamysis bahia*). The marine bacterium (*Vibrio fischeri*) is another frequently used test organism. A test system that measures changes in the luminescence of *V. fischeri*, known as Microtox, has been developed to provide a rapid and reproducible toxicity screening tool.

There is no single test method that can be recommended for toxicity measurements. Different species have different sensitivities to important contaminants, such as metals, PAHs, and pesticides. Differences in sensitivity have also been reported in studies of runoff toxicity (Tables 4.3 and 4.5). In general, crustaceans such as water fleas or amphipods are often more sensitive than fish or the Microtox system, but relative sensitivity among species can vary on a site-specific basis. Thus a battery of several test species is needed to provide assurance that important toxicants will be detected in the sample.

4.9.2 MEASURING TOXICITY IN SEDIMENT

Water phase tests provide a biological assessment of the short-term effects of the dissolved constituents of roadway runoff. These tests are generally insensitive to contaminants associated with the particulate fraction or those contaminants requiring several days to accumulate to toxic levels within the organism. A variety of sediment toxicity tests are available to evaluate the biological effects of materials associated with sediments. Sediment test methods fall into two categories. The first category is comprised of tests that expose the organism directly to the particulate fraction. These tests are usually conducted with amphipods or insect larvae over a period of 4 to 28 days, with survival and growth being the key endpoints measured [136,137].

Alternatively, sediment toxicity can be measured by testing a water phase prepared from the sample. This water phase can be interstitial water, sediment elutriate, or a solvent extract spiked into clean water. The water phase is then tested using the same methods used for the dissolved portion of a roadway runoff sample. The testing of water derived from sediments generally yields a greater degree of toxicity because the water phase test methods are generally more sensitive than those used for sediments. The results must be interpreted cautiously, however, because some preparation methods (e.g. solvent extraction) alter the biological availability of the contaminants and can over or underestimate the toxic potency of the sample.

Sediment toxicity methods that involve a minimum of sample manipulation are recommended, as these methods are most likely to represent the potential for toxicity in the environment.

4.9.3 TOXICITY MEASUREMENT IN THE FIELD

WET tests are based upon the continuous exposure of organisms to a constant concentration of the sample. This is an unrealistic exposure scenario for the majority of roadway runoff discharges, where the composition of the discharge may vary greatly over a span of minutes to hours, and the total exposure may last less than one day.

The biological response of organisms exposed in the field reflects the actual exposure conditions and therefore provides a more accurate assessment of impacts. Field assessments are more difficult to conduct and interpret, however, because confounding environmental variables may influence the results and it may be difficult to obtain representative control or reference samples with which to compare the results against. There are two general approaches to measuring roadway runoff effects in the field:

(1) toxicity tests using laboratory test species placed in cages in the receiving water (*in situ* exposure chambers) and (2) assessment of resident organisms or communities (biosurveys).

In situ exposure chambers. Several studies have measured the response of fish or invertebrates placed in cages in streams influenced by roadway runoff discharges (Figure 4.2). The exposure chambers usually consist of a transparent tube or box that has been modified with a screened opening to allow water exchange [124]. Placement of the chambers can be varied at the site to provide differing degrees of exposure to factors such as sediment and light. Organisms exposed in *in situ* chambers often show different responses compared to the same species exposed to a water sample from the site in the laboratory [130], indicating that laboratory tests do not replicate all-important aspects of the exposure.

Biosurveys. The sampling and analysis of resident organisms provides the most direct and accurate assessment of impacts from roadway runoff discharge. Samples of benthic organisms may be collected, counted, and identified to detect community-level changes. Changes in the abundance and composition of invertebrate species have been observed in streams downstream of roadway runoff discharges and in roadway runoff treatment ponds. It is difficult to associate community level changes with toxic constituents; however, because changes in sediment grain size and organic loading can produce similar changes. A more reliable method to assess the influence of roadway runoff discharges is to measure contaminant concentrations in resident organisms. Elevated concentrations of metals and PAHs have been measured in fish and invertebrates living in proximity to discharges of runoff from roadways or urban storm drains.
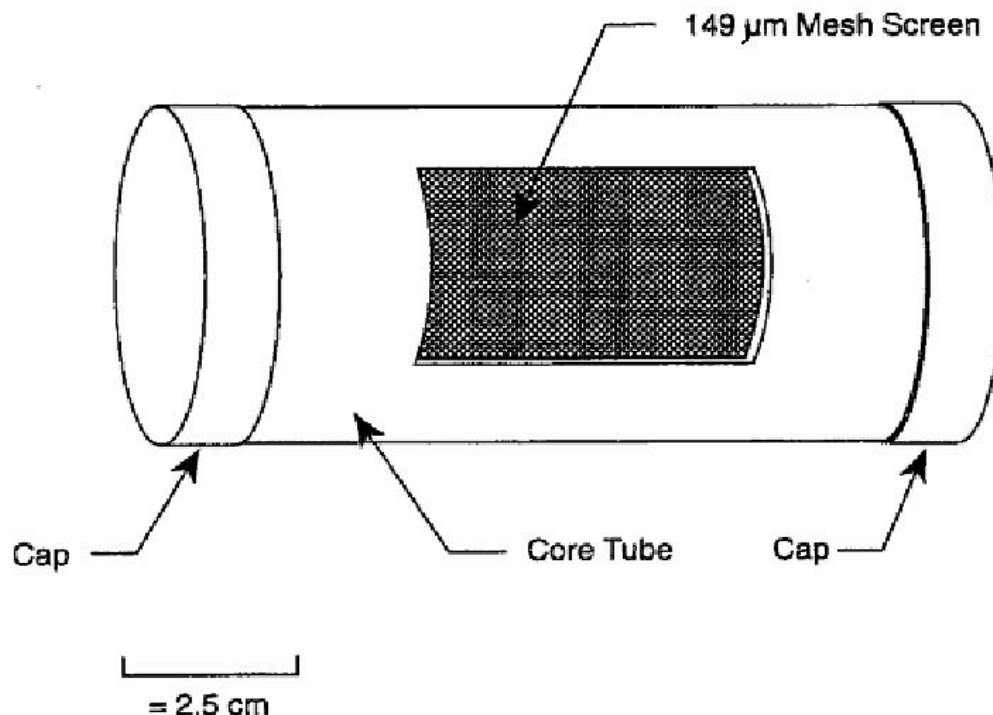
Figure 4.2
In situ chamber design (from Ireland et al. [124]).

4-13

4.10 IDENTIFYING CAUSES OF TOXICITY

Toxicity assessment is a critical part of any program to assess the biological impacts of roadway runoff. Tests with whole organisms or biochemical indicators provide an integrated assessment of the toxic effects of all constituents in a sample and help guide further analyses to determine toxic constituents. The value of the results of a bioassessment program is dependent upon its design, which should be developed in response to the objectives of the study. The objectives of the study must be considered before deciding on the location and frequency of sampling and before selecting the biological test methods. A toxicity testing program should be structured as a tiered approach. The first tier should consist of relatively inexpensive screening level tests to determine the approximate magnitude of toxicity.

More advanced second tier studies should then be conducted on samples with high or moderate levels of toxicity in order to more accurately determine the magnitude of toxicity, identify its cause and determine the sources within the watershed. The third tier of testing includes receiving water tests to confirm the laboratory toxicity results. This tier provides an opportunity to verify predictions that adverse receiving water impacts are occurring before expensive control measures are implemented.

4.11 IDENTIFICATION OF TOXIC CONSTITUENTS

The most productive approach for identifying the cause of roadway runoff toxicity is a sequential bioassay directed investigation, known as a toxicity identification evaluation, or TIE [138]. TIE methods were originally developed for use with wastewater effluents and have been shown to be effective in determining the toxic constituents of roadway runoff [27,139].

A complete TIE is a three-phase process consisting of steps to characterize the general nature of the toxicants, then identify and confirm the specific chemicals causing the toxicity (Table 4.6). These procedures are compatible with most water phase test species used to measure roadway runoff toxicity. TIE methods for sediment are still under development and no consistent approach is currently in use. Conventional TIE methods can usually be applied to sediment interstitial water; solvent extraction and fractionation of sediment contaminants to determine the toxic constituents can also be carried out [18].

Table 4.6

Toxicity identification evaluation (TIE) methods & purpose (adapted from U.S. EPA)

TIE Phase and Procedure	Purpose and Interpretation of Positive Result
Initial toxicity measurement	Establishes need for TIE
Phase I: Characterization	Determine broad chemical characteristics of toxicant
Baseline toxicity measurement	Reference to assess effectiveness of other treatments, stability of toxicity during storage
Filtration/centrifugation	Particle-associated toxicity
Aeration	Volatile, sublatable, or oxidizable toxicant
C18 Solid Phase Extraction	Nonpolar organic, metal chelates or surface active forms
EDTA (chelant) addition	Divalent cationic metal
Thiosulfate (reductant) addition	Oxidant or some cationic metals
pH adjustment	Stability/volatility/solubility is pH dependent
Graduated pH test	Potency/speciation is pH dependent
Phase II: Identification	Determine specific chemicals likely causing toxicity
Piperonyl butoxide (PBO) addition	Metabolic inhibitor that blocks action of organosphophate pesticides, may enhance activity of pyrethroid pesticides
C18 column elution and analysis	Confirmation and concentration of nonpolar organics
Fractionation of sample/eluate	Simplify complex mixtures to isolate toxicant
Chemical analysis	Identify likely toxicants in eluate or fractions
Phase III: Confirmation	Verify toxicant identification
Spiked sample testing	Confirms dose-response relationship and controls for sample matrix effects
Correlation of sample toxicity and chemical concentration	Verifies identification of toxicant
Toxic unit comparison	Presence of unidentified toxicant or matrix effects

TIE investigations of urban runoff usually identify metals (Zn, Cu) or organophosphorus pesticides (diazinon and chlorpyrifos) as the primary constituents of concern (Table 4.7). PAHs and particles have not been identified as a primary cause of toxicity in water phase tests conducted in the laboratory.

Table 4.7
List of identified toxicants in urban and agricultural runoff

Sample Type	Toxicants	Test Organism	Reference
Urban roadway runoff	Zn, Cu	Sea urchin	Bay *et al.* [122]
Urban roadway runoff	Zn, Cu	Sea urchin	SCCWRP [27]
Urban roadway runoff	Metals	Water flea	Hall and Anderson [141]
Urban roadway runoff	Diazinon	Water flea	SCCWRP [27]
Urban roadway runoff	Diazinon, Chlorpyrifos	Water flea	Lee and Taylor [140].
Urban roadway runoff	Metals	Microtox	Herricks and Milne [142]
Urban roadway runoff	Metals, neutral organics	Fish	Lopes and Fossum [123]
Urban roadway runoff	Diazinon	Water flea	Katznelson *et al.* [143]
Urban roadway runoff	Diazinon	Water flea	BASMAA [4]
Roadway runoff (sediment)	PAHs	Water flea	Maltby *et al.* [18]
Industrial roadway runoff	Metals	Water flea	BASMAA [4]
Asphalt pavement milling	Particles	Water flea	King *et al.*
Airport roadway runoff	Glycol deicers	Water flea, Fish	Fisher *et al.* [10]
Urban roadway runoff	Ammonia, suspended solids	Amphipod	Mulliss *et al.* [20]
Urban/Agricultural runoff	Diazinon, Chlorpyrifos	Water flea	DeVlaming *et al.* [128]
Urban roadway runoff (*in situ*)	PAHs	Water flea	Ireland *et al.* [124]

There have been few studies that have attempted to identify the cause of toxicity in runoff from roadways. The toxic components in sediments contaminated by roadway runoff was investigated using solvent extraction and fractionation [18]. These studies identified the PAH-containing fraction as toxic to amphipods. Toxicity to Microtox was associated with a different fraction, which contained aliphatic hydrocarbons. The toxicity of roadway runoff in the San Francisco Bay area was primarily sublethal in nature, suggesting that the cause was not pesticides and may have been metals [4]. Deicing chemicals have been identified as a potential source of toxicity from transportation land uses. Glycol compounds were identified as the cause of toxicity in airport roadway runoff [10] and the seasonal nature of roadway runoff toxicity observed by Marsalek et al. [16] suggests that road salts may have been a source of toxicity, either through the direct effects of ionic imbalance or due to solubilization of other contaminants by chlorides.

Asphalt paving compounds can generate toxicity through multiple mechanisms. The leaching of newly applied asphalt or sealants was associated with increased roadway runoff toxicity to fish and invertebrates [140]; toxicity from these compounds appears to decline markedly following leaching by rainfall. In addition, high concentrations of weathered asphalt in runoff can cause toxicity. High concentrations of particles from milled asphalt pavement caused toxicity to crustaceans and inhibited the successful hatching trout eggs. The toxicity was thought to be associated with the physical effects of the fine particles and no impacts considered likely at environmentally relevant concentrations.

PARTICLES AND CONTAMINANTS IN ROADWAY RUNOFF

5.1 SUMMARY OF FINDINGS

Particles in roadway runoff may harbor significant levels of toxic contaminants. In this chapter we review what is known about the relationship between particles and contaminants, and analytical methods that might be employed to better assess the role that particles play in mobilizing contaminants from roadway surfaces during storms. The primary findings described in this chapter are as follows:

- A large fraction of the heavy metal and non-polar organic contaminant load in roadway runoff is adsorbed to particles. Most BMPs for roadway runoff are designed to treat only the particulate fraction. Hence, toxicity and contaminant reductions by BMPs are limited by the degree to which pollutants/toxicity associate with particles, and the efficiency with which BMPs remove particles, both of which can vary with particle size.

- Measurement of particle-bound pollutants in roadway runoff involves three basic steps: solid/liquid separation, solubilization of particulate bound contaminants (digestion), and analytical measurement of the solubilized contaminants. While there are numerous procedures reported in the literature, there are no regulatory approved or standardized methods for measuring particle-bound contaminants in roadway runoff. Currently employed methods are adapted from methods used for soil, solid waste, and wastewater quality analyses.

- The concept of contaminant bioavailability is often used for toxicity prediction. However, no relationships or methods have been established to determine bioavailability of particulate contaminants. Although controversial, methods such as sequential extraction and acid volatile sulfides, used for contaminated soils and sediments, may be possible approaches to assess heavy metal bioavailability potential of roadway runoff contaminants.

5.2 TERMINOLOGY

A brief description of terms that are used in this chapter is summarized in table 5.1

Table 5.1
Terminology used in measuring particle-bound contaminants

Term	Description
Dissolved Organic Carbon (DOC)	Organic compounds that pass through a 0.45 μm filter, and typically include refractory compounds like humic and fulvic acids.
Humic substances	Humic substances are formed by the biochemical transformation of plant and animal residue, and constitute a major fraction of the dissolved and particulate organic matter in natural ecosystem.
MCL	Maximum Contaminant Level MCL are enforceable standards for drinking water.
MCLG	The level of a contaminant in drinking water below which there is no known or expected risk to health. MCLGs allow for a margin of safety and are non-enforceable public health goals.
PAHs	Poly Aromatic Hydrocarbons.
Polyelectrolyte	A *polyelectrolyte* is a macromolecular substance which, on dissolving in water or another ionizing solvent, dissociates to give *polyions* (*polycations* or *polyanions*). A polyelectrolyte can be a *polyacid*, a *polybase*, a *polysalt* or a *polyampholyt*.
SVOC	Semi volatile organic compound.
VOC	Volatile organic compound.

5.3 CONSTITUENTS IN ROADWAY RUNOFF

Constituents in roadway runoff range from Dissolved Organic Carbon (DOC) at the small end of the size spectrum (1 to 10 nm), dust and tire-derived particles at intermediate sizes (1 to 100 μm), and trash and debris at the large end (10cm to 1m). These materials vary enormously relative to their physical and chemical properties, and their tendency to bind and transport pollutants from roadways during storms.

It is estimated that more than 50 percent of the DOC in surface-and groundwater consist of refractory polyelectrolytes [144]. In general, aquatic humic substances are complex mixtures of related macromolecules of varying composition, structures, functionalities and molecular masses. Due to their structural variability, humic substances are involved in many environment processes [145] especially in binding, transport and deposition of inorganic and organic pollutants including heavy metal ions. Natural macromolecular materials, including humic substances, found in natural waters are thought to be loosely wound, flexible molecular strands whose conformation strongly depends on pH and electrolyte concentration. Hence, the size of dissolved macromolecules can range from full molecular expansion at small electrolyte concentration to dense collapsed structures at high ionic strengths.

5.4 HEAVY METALS IN ROADWAY RUNOFF

Heavy metals in roadway runoff can adversely affect receiving waters by increasing toxicity in the water column and/or sediments, and bioaccumulating in the food chain. The most often cited heavy metal contaminants are Cd, Cr, Cu, Fe, Ni, Pb, and Zn. Although there are significant metal-dependent and study-dependent variabilities, in general it can be said that a significant fraction of the heavy metals found in runoff maybe associated with the suspended solids (i.e. adsorbed to particles)[82]. Sources of metals in roadway runoff include traffic deposition (e.g., tire wear, brake linings leakage of oil and lubricants), dust from the surrounding environment, pavement wear (the breakdown of asphalt and/or concrete surfaces), maintenance operations (e.g., application of deicing compounds, pesticides and herbicides), accidental spills, and littering (Table 5.2) [146].

Table 5.2
Primary sources of heavy metals in roadway runoff [147].

Constituents	Sources
Aluminum	Natural, as well as anthropogenic sources such as aluminum works industries
Cadmium	Tire wear, brake pads, combustion of oils, insecticides are also other sources.
Chromium	Corrosion of welded metal plating, moving engine parts, brake lining wear
Cobalt	Wastes from tire and vehicle appliance manufacturing
Copper	Metal plating, bearing and bushing wear, moving engine parts, brake lining wear, fungicides and insecticides
Iron	Auto body rust, steel roadway structures, moving engine parts, corrosion of vehicular bodies
Lead	Leaded gasoline, tire wear
Nickel	Diesel fuel and gasoline, lubricating oil, metal plating, bushing wear, brake lining wear, asphalt paving
Zinc	Tire wear, motor oil, grease

Total heavy metal concentrations (dissolved + particulate), and other pollutant parameters, in roadway and urban runoff are summarized in Table 5.3. For comparison, drinking water standards for the various constituents are also included. The primary results are summarized below.

Cadmium, has been measured in roadway runoff at concentrations ranging from non-detectable to 13.7 mg/L, and is present in both the dissolved and colloidal fractions [17]. The drinking water standard for Cd is 0.005 mg/L.

Chromium, has been measured in roadway runoff at concentrations ranging from 0.001 to 2.3 mg/L. Chromium is soluble, mobile, and can be stable for long periods in waters with low levels of organic matter; Cr can also form stable complexes, especially

chromium hydroxide [17]. The drinking water standard for Cr is 0.1 mg/L. It was detected in 58 percent of the National Urban Research Program (NURP) priority pollutant study samples.

Cobalt, has been measured in roadway runoff at concentrations ranging from 0.05 to 13.73 (µg/L). There are no drinking water guidelines or aquatic criteria for cobalt.

Copper, has been measured in roadway runoff at concentrations ranging from 0.00006 to 1.41 mg/L; and is typically associated with dissolved solids and colloidal material [17]. The maximum concentration level goal (MCLG) for copper in drinking water is 1.3 mg/L. Although copper often does not exceed this limit, it is still considered a toxic metal of significant concern in storm water; this metal was detected in 91 percent of the NURP priority pollutant study samples [17].

Iron, has been measured in roadway runoff at concentrations ranging from 0.13 to 440 mg/L; and is primarily associated with suspended solids [17]. The secondary (aesthetic) drinking water standard for iron is 0.3 mg/L.

Lead, has been measured in roadway runoff at concentrations ranging from 0.000053 to 26 mg/L; and is mostly associated with suspended solids or as a carbonate precipitate[17]. The reported roadway concentrations for lead exceed all drinking water guidelines and regulations.

Nickel, has been measured in roadway runoff at concentrations ranging from 0.00006 to 49 mg/L. Like most of the metals, there is a strong correlation between nickel, suspended solids, and organic matter. Nickel was detected in 43 percent of the NURP priority pollutant study samples.

Zinc, has been measured in roadway runoff at concentrations ranging from 0.0007 to 22 mg/L. However, unlike most metals, zinc is mostly associated with the dissolved fractions, although it can also adsorb to suspended sediment and colloidal particles. Zinc was detected in 94 percent of the NURP priority pollutant study samples.

Table 5.3
Heavy metals, and organic pollutants in roadway runoff

Parameter	Roadway runoff	Urban runoff	Drinking water standard (MCL)[a], mg/L	Reference[b]
Heavy metals (µg/L)				
Cadmium	0.17 -12	0.02 - 13,730	0.005	17,146,48,160,22,162,161,82,122,32, 163,43,79,60,164,36
Chromium	1.5 -110	1 - 2,300	0.1	17,146,48,160,162,163,12,88,164,165
Cobalt	0.05 -13.7	1.3 - 5.4		17,146
Copper	3-1,200	0.06 - 1,410	1.3	17,146,48,160,22,162,161,82,122,166, 171,2,42,32,3,163,43,79,33,60,88,164,167, 168
Iron	130-45,000	0.07 -440,000	0.3	17,173,146,48,160,162,177,166,9,29,163, 167,168,165,36, 174
Lead	3-2,100	0.053 -26,000	Zero	17,7,146,48,160,162,161,175,176,177,82, 122,171,172,83,2,42,32,3,163,43,79, 169,12,60,88,164,167,168,165,36, 174
Nickel	1 - 57	0.06 - 1,410		17,173,146,162,163,88,164
Zinc2	10 - 1,200	7 - 4,600	5.0	17,7,173,146,48,160,22,161,175,176, 82,148,166,170,19,2,9,29,32,3,163,43,169, 12,88,164,167,168,165,36, 174
Mercury	0.076 - 5.6	0.05 - 67	0.002	17,146
Aluminum	30 - 4,000	1 - 49,000	0.05-0.2	17,146,164
Organic chemicals				
Total PAH (mg/L)	1.86 - 18.2	2.4E-4 - 1.3E-2	0.0002[c]	17, 48,79, 81
Benzo(pyrene)		2.5E-6- 1E-2	zero	17,163
Fluoranthene		3E-5 - 5.6E-2	3.96	17
Naphthalene		3.6E-5 - 2.3E-3	0.62	17
Phenanthrene		4.5E-5 - 1E-2		17
Tetrachloroethylene		0.0045 - 0.043	zero	17
Heptachlorepoxide		<0.0002	zero	17
Oil and grease	<1 - 480	0.001 - 110		17, 81

[a] Maximum contaminant levels for drinking water quality , as of the Federal Register dated March 21 , 2000
[b] References are for roadway runoff
[c] U.S. aquatic regulation (freshwater chronic)

5.5 NON-POLAR ORGANICS IN ROADWAY RUNOFF

Non-polar organic contaminants are very likely to be associated with particles in roadway runoff, due to their hydrophobic character. Semi-volatile organic compounds (SVOCs) and volatile organic compounds (VOCs) are two groups of contaminants that have been measured in runoff from roadways and urban areas (Lopes and Dionne 1998). VOCs are present in many products including fuels, solvents, paint, and vehicle exhaust [81]. However, they are not routinely detected in roadway runoff. This is most likely due to their volatility and favorable mass transfer conditions during storm events.

Petroleum and hydrocarbons from spills/leaks, oil and grease, and vehicle emissions are the major SVOCs detected in roadway runoff and urban storm water. Gasoline exhaust contains about 1 to 2 parts per million of phenol and o-cresol and is a possible source of phenolic compounds in storm water [81]. Another source of PAHs is leaching from creosoted wood products such as railway ties and telephone poles. Reported loading factors of SVOC from roadways are summarized in Table 5.4.

The most commonly reported class of organic compounds in roadway and urban runoff is SVOCs [81]; this class includes polycyclic aromatic hydrocarbons (PAHs). About 80 percent of SVOCs in runoff are in the suspended solids [81]. Once PAH-laden suspended solids in runoff reach the final receiving water, they settle and contaminate receiving water sediments. In a German study of roadway runoff, it was found that only 14 percent of the total PAH was in dissolved forms [11]. PAHs in stream sediment adjacent to roadways have been shown to have a high potential for adverse effects on receiving streams [6,18,81].

The largest analysis of organic chemicals in storm water was conducted during the National Urban Research Program (NURP) study. Of the 106 organics tested for, 63 compounds were found in storm water. Certain PAHs, phenol, *m*- and *p*-cresols, pentachlorophenol, and phthalates were of particular concern due to their potential impact on receiving waters and aquatic life [81]. Fluoranthene, naphthalene, phenanthrene, and pyrene were detected in 10 to 12 percent of the urban runoff samples [7]. Total PAH, acenaphthene, fluoranthene, and benzo(a)pyrene in urban storm water exceeded drinking water standards. Concentrations of fluoranthene in storm water exceeded acute and chronic aquatic regulation values of the United States [81]. The concentrations of individual PAHs in runoff ranged from less than 1 to 56 µg/L (see Table 5.3). However, maximum observed concentrations of total PAHs were on the order of 18,000 µg/L. Data on PAH concentrations in roadway runoff are very limited.

Table 5.4
Loading factors for semi volatile organic compounds (SVOCs) in roadway runoff [81]

Compound class	Loading rates from roadways
Petroleum hydrocarbons	7800 $(kg/km^2)/yr$,
	2.5E-5 (kg/vehicle)/km,
	126 (kg/km^2)/cm rain
Oil and grease	485-700 $(kg/km^2)/yr$
	9 - 16 (kg/km^2)/event
	27 - 298 (kg/km^2)/cm rain
PAHs	[a]1.22 $(kg/km^2)/yr$
	[b]16.9 $(kg/km^2)/yr$
	5.8E-8 (kg/vehicle)/km
	0.151 (kg/km^2)/cm rain

[a] Low molecular weight PAHs
[b] High molecular weight PAHs

5.6 MEASUREMENTS OF PARTICLE-BOUND CONTAMINANTS IN ROADWAY RUNOFF

Summaries of dissolved and particulate phase heavy metal concentrations in roadway runoff are presented in Tables 5.5, 5.6. In these studies, the boundary between "dissolved" and "particulate" was defined operationally by filtration through a 0.45 μm filter. Copper, lead and chromium appear to be more strongly associated with the particulate fraction, at least compared to zinc and cadmium. Particulate concentrations of selected metals, Zn, Pb, Cd and Cu as a function of particle size in runoff samples are presented in Table 5.7. For Zn, Pb and Cu the concentrations generally increase with increasing specific surfaces area (SSA) or decreasing particle size. However, there is no obvious relationship between cadmium and SSA based on the upper concentration range associated with each size fraction. Based on the data presented in Table 5.7, metals are primarily associated with the finer particle sizes, less than 150 microns. This observation suggests that sedimentation basins, and perhaps even filtration systems, may be ineffective at removing metals from roadway runoff.

With respect to non-polar organics, namely PAHs, the situation is more complex. Particulate concentrations of selected PAHs and organic carbon as a function of particle size in runoff samples are presented in Table 5.8. Although there is no universal trend, it appears that for some of the PAH species, concentration increases with increasing particle size, opposite the trend observed for metal contaminants.

Table 5.5
Dissolved and particulate phase pollutant concentrations in 13 storm events [79].

Constituent	Concentration range, µg/L[a]		Total[b]	Particulate % Total
	Dissolved phase	Particulate phase		
Cadmium	0.05 – 12 (**1.3 ± 1.7**)	0.1 - 7.2 (**1.7 ± 1.4**)	3.0	57
Copper	3.6 – 39.2 (**16.1 ± 59**)	13.1 – 145 (**47 ± 24**)	63	75
Lead (total)	8 – 46.5 (**16 ± 69**)	39 – 482 (**165 ± 101**)	181	92

[a]Numbers in bold are mean ± Standard Deviation
[b]Mean

Table 5.6
Dissolved and Particulate Metal Concentrations in Runoff [82]

Metal	Dissolved fraction, mg/L	Particulate fraction, mg/L	Percent in particulate fraction
Zinc	0.21 - 3.8	0.17 - 0.64	11 - 46
Cadmium	0.002 - 0.2	0.002 - 0.004	18 - 60
Copper	0.013 - 0.1	0.03 - 0.1	3 - 69
Nickel	0.005 - 0.07	0.02 - 7.4	44 - 95
Lead	0.005 - 0.024	0.05 - 0.09	26 - 97
Chromium	0.006 - 0.03	0.03 - 0.008	29 - 74
Iron	0.043 - 0.59	0.78 - 6.12	85 - 98
Aluminum	0.006 - 0.432	0.004 - 1.8	40 - 90

Table 5.7
Percentage distribution of metals as a function of particle size fractions in roadway runoff [52]

Metal	Particle Size, µm										
	4,750-9,500	2,000-4,750	850-2,000	425-850	250-425	150-250	75-150	63-75	45-63	38-45	25-38
Zinc	0.2-1	1-2	1-4	3-5	3-5	6-9	13-16	14-18	14-16	14-19	17-19
Lead	0.2-1	1-14	1-5	2-5	3-6	6-13	14-20	14-19	14-19	13-16	13-20
Cadmium	1-17	9-11	6-9	5-9	5-6	5-7	9-11	10-12	10-13	10-13	9-12
Copper	0.2-1	0.5-1	0.5-3	1-23	2-9	4-13	11-15	11-17	11-19	12-19	15-24

Table 5.8
Concentration (μg/g) of selected PAHs and organic carbon content as a function of particle size in roadway runoff [46]

Constituent	Particle size fraction, (μm[a])					
	<2	2 - 6.3	6.3 - 12.5	12.5 - 20	20 - 63	63 - 200
Fluorene	2 ± 1.1	47 ± 2.1	51 ± 2.5	60 ± 2.6	32 ± 1.5	74 ± 3.3
Anthracene	24 ± 1.2	61 ± 3.1	65 ± 3.3	72 ± 3.2	64 ± 3.3	147 ± 7.4
Phenanthrene	183 ± 7.7	733 ± 37.5	763 ± 37.7	766 ± 34.3	580 ± 23.2	1022 ± 52.1
Fluoranthene	350 ± 16	1622 ± 83	1554 ± 67.6	1155 ± 48.7	1078 ± 39.9	1958 ± 93.3
Indeno(cd)pyrene	86 ± 3.8	402 ± 22.2	271 ± 12.6	76 ± 3.2	127 ± 5.4	146 ± 6.8
Dibenz(ah)anthracene	20 ± 0.9	83 ± 3.8	66 ± 3.5	11 ± 3.9	34 ± 1.8	41 ± 2.1
Benzo(ghi)perylene	139 ± 6.9	710 ± 31.9	541 ± 27.8	217 ± 9.8	287 ± 12.3	281 ± 13.7
Organic carbon	14 ± 0.1	22 ± 0.3	25 ± 0.2	27 ± 0.3	19 ± 0.1	30 ± 0.2

[a] Values are presented as mean ± standard deviation

5.7 METHODS FOR ESTIMATING PARTICULATES BOUND CONTAMINANT LOAD

There are two basic approaches for estimating the contaminant load associated with particulates in roadway runoff. The first approach is a simple differential method in which contaminant concentrations of both whole and filtered samples are determined. The difference in concentration between these two measurements is assumed to be the particulate contaminant fraction. The second approach involves desorbing or solubilizing the contaminants from the particulates, and then measures the pollutant load. Both of these approaches may be used simultaneously, or individually. Further, both approaches require a solid/liquid separation step. A flowchart of this basic methodology is shown in Figure 5.1.

Although the concept of two contaminant phases, particulate and soluble, appears to be relatively simple, it is not. As noted previously, silts and colloids, which have particle sizes ranging from 1 to 50 μm and 0.001 to 1 μm, respectively, have high sorption capacities for heavy metals and non-polar organics [52,46]. Thus, silts and colloids are the most likely particles to have toxicity associated with them. Unfortunately, with the exception of the larger silt particles, only a small percentage of the particles in these size ranges will be removed by a BMP solids/liquid separation treatment system such as a sedimentation tank or sand filter without a chemical aid to promote aggregation. However, silt and colloidal particles will eventually aggregate and settle in a receiving water body, especially the ocean. Therefore, the "particulate" fraction can be viewed from several perspectives. Firstly, the particulate fraction can be defined as those solids

that can be removed by a specific BMP process, or characterized by a specific cutoff size. Particles larger than a specific size, or those removed by a specific process, are considered particulate. Those smaller than a specific size, or not removed by a specific process, are considered dissolved. Using this approach, the specific cutoff size or separation process that delineates "particulate" and "soluble" must be defined methodologically. *Standard Methods for the Examination of Water and Wastewater* [66] uses the terms "settleable" and "suspended" to define solids that are separated by a standardized sedimentation apparatus, an Imhoff cone, and solids separated by a specific filter paper, Whatman 934AH (nominal pore size = 1.5 µm) or its equivalent, respectively. (It should be noted that a portion of the solids defined as "suspended" in *Standard Methods* are not removed in a sand filter.)

Runoff

Dissolved/particulate separation

Fractionation

Particle sizes
categories

Metals   **Organics**

Digestions

Extractions

Analyses

Analyses
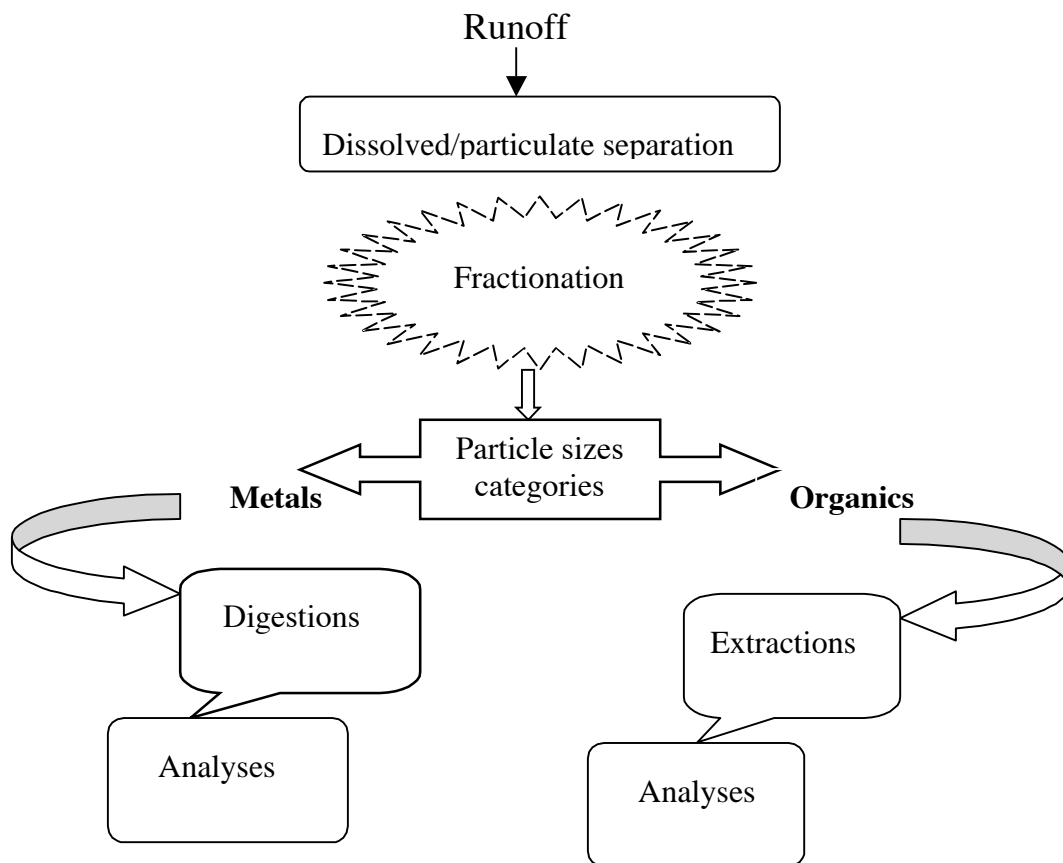
Figure 5.1
General procedure for measuring the concentration of particle-bound organic and inorganic pollutants.

The particulate fraction may also be defined as those solids that will become sediment in a receiving water body. In this case, the particulate fraction of concern will depend on the nature of the specific receiving water body including its velocity and temperature profiles, and its chemistry. In this approach, particles must be defined by a number of

parameters including size distribution, stability relative to coagulation and fragmentation, and settling rates. This second approach lends itself to the Gustafsson and Gschwend (1997)[93] classification discussed in Chapter 1 in which the contaminant pool is divided into dissolved, colloidal, gravitoidal, and sediment fractions. To date, there have been a limited number of studies that have investigated particulate contaminant distributions. Of these limited studies, most of the emphasis has been on contaminant distribution by particle size, which partially addresses both of the perspectives outlined above.

5.8 SOLID/LIQUID SEPARATION AND SIZE FRACTIONATING PARTICLES IN ROADWAY RUNOFF SAMPLES

Solid/liquid separation processes used in practice include sieving, centrifugation, and membrane filtration. These traditional particle fractionation methods, together with emerging technologies, were reviewed and described previously in section three of this report.

5.9 HEAVY METAL ANALYSIS

After solid/liquid separation of roadway has been conducted, the captured particulates, either in total or in various size fractions, can be analyzed for sorbed heavy metals or organics. Heavy metal analysis requires solubilization of the sorbed metals via digestion. Digestion techniques vary widely but almost always utilize strong acids under elevated temperatures to bring metals into solution. Reported digestion techniques used in roadway runoff studies are outlined in Table 5.9.

Once solubilized via digestion, the heavy metal concentration is determined by instrumental analysis using atomic absorption (AA) spectroscopy [14,35,46,55,110,149] or inductively coupled plasma (ICP) spectroscopy [11,29,56].

5.10 BIOAVAILABLE FRACTION OF PARTICULATE HEAVY METALS

One problem associated with digestion methods for soils and sediments is that metals associated with the mineral component of the soil or sediment may be brought into solution as well. Thus, metal concentrations determined using digestion techniques could overestimate the extent and potential toxicity of particulate metal pollutants. For this reason, over the past 20 years, researchers have been investigating methods to estimate the "bioavailable" fraction of the total particulate metal concentrations in soils and sediments, as well as other solid matrices. Although a standard methodology has yet to be agreed upon, there are two basic approaches used to assess bioavailability and potential toxicity in soils and sediments: (1) sequential extractions and (2) the relationship between acid-volatile sulfides (AVS) and simultaneously extracted metals (SEM). To the authors' knowledge, these two methods have not been applied to roadway runoff.

Table 5.9
Digestion methods for heavy metal analysis used in roadway runoff studies

Method	Description	References
Method 3030F (APHA, 1989)	Sample material digested using strong the nitric acid-hydrochloric acid reagent.	Lygren et al. (1984)[35]
		Characklis and Wiesner (1997)[56]
		Krein and Schorer (2000)[46]
Dutch Standard Method NEN 6465[a]	Sediments dried at 60°C for a minimum of 60 hours, then subjected to acid digestion with HCL/HNO_3 (3:1) at 250°C.	Bijlsma et al. (1996)[55]
Method 3015 and 6010 (USEPA, 1990)	Microwave digestion based on SW-846.	Sansalone and Buchberger [82]
		Sansalone and Buchberger [52]
Strong acid digestion	Sample baked at 550°C then digested in a mixture of concentrated hydrochloric and hydrofluoric acids.	Colandini et al. (1995)[110]
		Legret and Pagatto (1999)[14]
Microwave digestion	Microwave digestion in digestion bomb with aqua regia	Shinya et al. (2000)[29]

[a]Used to study the distribution of heavy metal pollution of canal sediments

5.10.1 Sequential Extractions

Sequential extraction methods have been applied to assess leaching potential of metals from soils and sediments, nutrient availability for plants, and prediction of fate and mobility of metals from soils and sediments. There is a relatively extensive body of literature pertaining to sequential extraction methods. The basic idea behind these techniques is that the particulate phase of a sample is treated with a series of progressively more aggressive extraction steps to isolate different metal-bound fractions in the sample. Some steps involve ion exchange and displacement while others involve oxidation/reduction dissolution.

Researchers have developed a wide variety of sequencing schemes and extracting reagents to study specific metal-binding mechanisms. The most often cited work is that of Tessier et al. [150]. They defined five metal-binding fractions (1) exchangeable, (2) carbonate bound, (3) Fe-Mn oxide bound, (4) organic bound, and (5) residual (mineral phase) fraction. The strength of the metal-solid binding increases with each sequential phase. Thus, metals in exchangeable and carbonate-bound fractions are more readily solubilized than organic or Fe-Mn oxide bound fractions. The underlying hypothesis is that the fractions of metals that are more easily solubilized pose more of an environmental threat through their mobility, bioavailability, and toxicity. Apart from the

pioneering work of Tessier et al. [150], other examples in the literature where sequential extractions have been employed include: 39,151-158.

5.10.2 Acid-Volatile Sulfides and Simultaneously Extracted Metals

In 1995, an EPA advisory board reviewed research and data to evaluate the use of acid volatile sulfide (AVS) and interstitial water concentrations of cadmium, copper, lead, nickel, and zinc to predict the bioavailability of these metals in sediments. For this approach, AVS, a principal binding phase for divalent metals, is quantified using a cold acid extraction method. The simultaneously extracted metals (SEM) from this cold acid extraction are compared to the concentration of AVS. If the molar concentration of AVS is greater than the molar concentration of SEM, metals associated with the particulate phase are assumed to be bound and hence not bioavailable.

Based on its review, the advisory board concluded that the SEM/AVS approach is the best technology available for assessing the significance of the five metals in sediments. They did, however, identify some limitations to the application of the methodology and additional research that would be required to support the development of metals criteria. A complete discussion of the advisory board's findings and recommendations is published in a report entitled *An SAB Report: Review of the Agency's Approach for Developing Sediment Criteria for Five Metals,* (EPA-SAB-EPEC-95-020, 1995). Based on the advisory board's recommendations, EPA has initiated the development of sediment criteria for the five metals mentioned above.

5.11 ORGANIC ANALYSIS

As with heavy metal analysis, organic analysis requires solubilization of the sorbed contaminants associated with the roadway runoff particulates. Organic extraction techniques vary widely but almost always utilize organic solvents to bring organics into solution. Reported organic extraction techniques used in roadway runoff studies are summarized in Table 5.10.

Table 5.10
Extraction methods for organic analysis used in roadway runoff studies

Method	Description	References
USEPA Method 3540C-Soxhlet extraction	Solvent extraction with (1:1) acetone/hexane mixture using a Soxhelt apparatus.	Drapper et al. (2000)[6]
		Krein and Schorer (2000)[46]
		Prytula and Pavlostathis (1996)[14][a]
Ultrasonic extraction	Extraction using acetonitrile and waters Step-pak plus PS2 cartridge.	Shinya et al. (2000)[29]
DMSO liquid extraction[b]	Using dichloromethane/acetone (95/5) and a DMSO liquid.	Macrae and Hall (1998)[159]
Dichloromethane extraction (Distol grade)	Using Distol grade dichloromethane (DCM) for 6 h.	Boxall and Maltby (1995)[18]
Gradient control extraction	Using gradient control (40:60 acetonitrile:water to 100% acetonitrile.	Hewitt and Rashed (1992)[79]
US EPA, 1979		

[a]Five extraction methods were used for contaminated estuarine sediment
[b]Used to estimate the available fraction of PAH in marine sediment slurries

Once solubilized the organic concentrations are determined by gas or liquid chromatographic methods [6,18,29,14,35,46,81,111,158].

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Appendix to Accompany:
A REVIEW OF THE CONTAMINANTS AND TOXICITY ASSOCIATED WITH PARTICLES IN STORMWATER RUNOFF
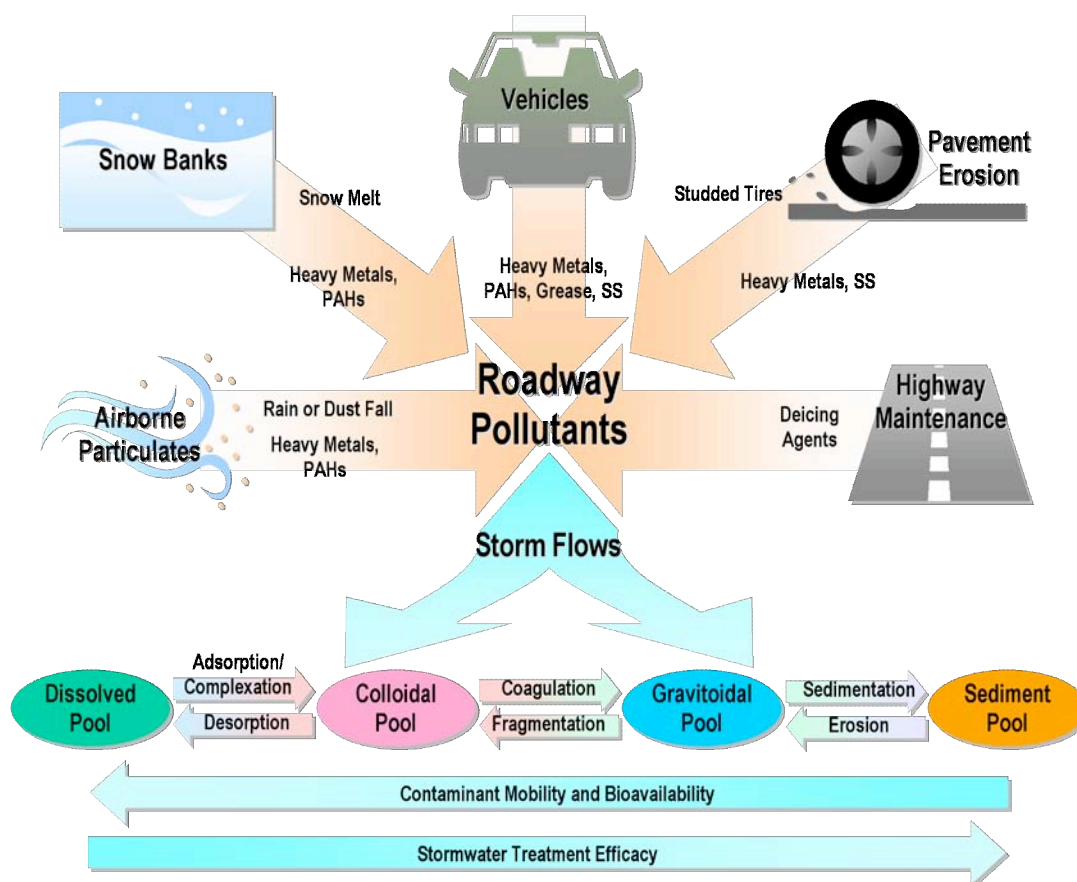
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This appendix presents an annotated bibliography of journal articles and reports reviewed as part of the project. The goal of the annotated bibliography is two-fold: (1) to provide short summaries of key content relevance to Caltrans' effort to control stormwater pollution, and (2) to serve as a reference list for some of the key citations that appear in the body of the report. Major emphasis was given to reviewed published articles and special efforts were given to include all relevant articles. If we missed any, that was unintentional.

Each summary consists of a short description of the paper's basic findings, a listing of keywords that reflect the article's content, and a short description of the article's related to stormwater treatment implications. If an article is focused exclusively on method development, the "stormwater treatment implication" category was not included.
The literature presented in this appendix can generally be grouped under one or more of the following categories (1) the measurement of toxicity in stormwater, (2) measurement of heavy metals and organic constituents in stormwater,(3) measurement of particle size distributions in stormwater, and (4) field investigations of stormwater runoff. For practical purposes these literatures are presented in alphabetical order .

1. **Ahyerre, M., G. Chebbo, B. Tassin and E. Gaume. "Storm water quality modeling, an ambitious objective?" Water Science and Technology, vol. 37(1), 205-213, (1998).**

   Pollutant fate and transport during storm is difficult to model due to the complexity of the underlying processes, uncertain mathematical formulations, and the cost of calibration. As a result, storm water quality models are not widely used as an urban pollution management tool. Simple models with a few parameters make better management tools than complex models.
   Keywords: Sewer quality modeling, urban pollution management, model calibration, sampling uncertainties.
   Stormwater Treatment Implications: Storm water quality models are currently of limited use for managing urban storm pollution.

2. **Ahyerre, M., G. Chebbo, M. Saad. "Nature and Dynamics of Water Sediment Interface in combined Sewers." J. Environ. Eng. (Reston, Va.) ,127(3), 233-239, (2001).**

   Suspended solids concentration profiles were measured at a set of locations within the combined sewer network of Le Marais district of Paris, France. The authors describe a novel method for visualizing the sediment/water interface, and discover the presence of a thick organic layer that contains a high concentration of particles. Authors also determine shear velocity μ in the sewers using both measured velocity profiles and acoustic Doppler current measurements. It was shown that at locations in the sewer network where shear stresses are <0.1 N/m^2 this organic layer can accumulate at the rate of 215 $g/(m^2\ day)$. Mass balance calculations and pollutant analyses of stormwater discharges indicate that these accumulations can contribute significantly to the pollution levels observed in stormwater discharges.
   Keywords: Waste Treatment and Disposal; combined sewer water sediment interface dynamics; org matter load combined sewer water sediment interface; volatile solids load combined sewer water sediment interface; surface water pollution urban storm water runoff.
   Stormwater Treatment Implications: The erosion of pollutants accumulated in runoff networks during low flow periods could significantly contribute to contamination of runoff discharges even for small rainfall events.

3. **Aiken, G.R., D.M. McKnight, R.L. Wershaw and P. MacCarthy (Eds.). "Humic Substances in Soil, Sediment and Water." Wiley, New York, (1985).**

   This book provides a comprehensive and critical review of the nature and function of humic substances in aquatic environments. The chemical nature of natural organic matter, and its role in pollutant transport, are considered.
   Keywords: Humic substances, geochemistry, isolation, fractionation, characterization
   Stormwater Treatment Implications: A useful reference for understanding the role that natural organic matter may play in pollutant mobilization.

4. **Andral, M.C., S. Roger, M. Montrejaud-Vignoles, L. Herremans. "Particle size distribution and hydrodynamic characteristics of solid matter carried by runoff from motorways." Water Environmental Research, vol. 71(4), (1999).**

 Sediment was collected from two sources along a highway in the Kerault region of France: (1) sediments accumulated in a collecting basin and (2) suspended solids present in storm water generated during eight storm events in 1993 and 1994. Both suspended and sediments were analyzed for PSD and mineral content; suspended sediments were additionally analyzed for TSS, mineral content, and heavy metals. For the fraction of the sediment below 100 μm in size, the PSDs and settling velocity distribution for the settled and suspended particles were remarkably similar. However, 90% of the sediment accumulated in the collecting basin had diameters larger than 100 μm. The authors conclude that the collecting basin acts like a decanter, removing particles greater than 100 μm. The majority of heavy metals (96%, 90.2%, 98.4%, 91.6%, 94.5%, and 100% for Zn, Pb, Cu, Cr, Ni, and Cd, respectively) are in the size range less than 100 μm.

Keywords: Runoff pollution, sedimentation speed, mineral content, density, particle size.

Stormwater Treatment Implications: >90% of heavy metals are associated with small particles (<100 μm). Hence, treatment schemes may need to focus on the removal of the finest particles. Paper also presents empirical relationships between settling velocity and particle density vs. particle size, which could be useful in designing BMPs. Furthermore, authors note that the density of particles decreases with decreasing particle size, presumably due to the higher organic content of smaller particles.

5. **Arnold, C.L., C.J Gibbons. "Impervious surface coverage, the emergence of a key environmental indicator." Journal of the American Planning Association. Vol. 62, No. 2, 243-258, (1996).**

This article argues that runoff from impermeable surfaces (e.g. pavement) is a leading threat to surface water quality. Watersheds with an impervious surface coverage greater than 10% experience impacted stream health; stream health degrades significantly when the watersheds impervious coverage exceeds 30%. Suggested solutions to this problem range from minimizing office-parking spaces to specific landscape architecture that would trap and process sediment and pollutants in runoff.

Keywords: Water resources; impervious surface coverage, runoff, pollutants, urban planning.

Stormwater Treatment Implications: Urban planning which minimizes impervious surface coverage and encourages the retention of stormwater in permeable surfaces could reduce the need for excessive stormwater treatment prior to discharge.

6. **Arthur, S. and R. Ashley. "The influence of near bed solids transport on first foul flush in combined sewers." Water Science and Technology, vol. 25(8), 1-12, (1998).**

 Field water quality data is presented for combined sewer outlets in Dundee, Scotland. For the three test sites investigated, the inorganic particle diameters ranged

from 0.09-11.0 mm, bulk density 1000-1998 kg/m^3, volatile solids 1.4-91.2 %, average COD 87522-214000 mg/L, average BOD 28594-96119 mg/L, and average ammonia 181-248 mg/L. It was concluded that while near bed solids have significant BOD and COD concentrations, they only account for a modest amount of the total solids actually transported. A mathematical model developed by the authors predicts the rate of solid transport to a reasonable degree of accuracy.

Keywords: Bed-Load; Combined Sewer; First Foul Flush; Near Bed Solids; Pollution Impacts; Sediment Transport; Sewer Sediment.

Stormwater Treatment Implications: Sediment build-up in combined sewer systems poses a serious pollution threat to receiving waters.**ASTM B330-88(1993) e1** Standard Test Method for Average Particle Size of Powders of Refractory Metals and Their Compounds by the Fisher Sub-Sieve Sizer.

7. **ASTM B430-97** Standard Test Method for Particle Size Distribution of Refractory Metal Powders and Related Compounds by Turbidimetry.
8. **ASTM B761-97** Standard Test Method for Particle Size Distribution of Refractory Metals and Their Compounds by X-Ray Monitoring of Gravity Sedimentation.
9. **ASTM B821-92** Standard Guide for Liquid Dispersion of Metal Powders and Related Compounds for Particle Size Analysis.
10. **ASTM B822-92** Standard Test Method for Particle Size Distribution of Metal Powders and Related Compounds by Light Scattering.
11. **ASTM B859-95** Standard Practice for De-Agglomeration of Refractory Metal Powders and Their Compounds Prior to Particle Size Analysis.
12. **ASTM C1070-86e1** Standard Test Method for Determining Particle Size Distribution of Alumina or Quartz by Laser Light Scattering.
13. **ASTM C1182-91(1995)** Standard Test Method for Determining the Particle Size Distribution of Alumina by Centrifugal Photosedimentation.
14. **ASTM C1282-94** Standard Test Method for Determining the Particle Size Distribution of Advanced Ceramics by Centrifugal Photosedimentation.
15. **ASTM C690-86(1997)e1** Standard Test Method for Particle Size Distribution of Alumina or Quartz by Electric Sensing Zone Technique.
16. **ASTM C721-81(1997)e1** Standard Test Method for Average Particle Size of Alumina and Silica Powders by Air Permeability.
17. **ASTM C958-92(1997)e1** Standard Test Method for Particle Size Distribution of Alumina or Quartz by X-Ray Monitoring of Gravity Sedimentation.
18. **ASTM D1366-86(1997)** Standard Practice for Reporting Particle Size Characteristics of Pigments.
19. **ASTM D1705-92** Standard Test Method for Particle Size Analysis of Powdered Polymers and Copolymers of Vinyl Chloride.
20. **ASTM D1921-96** Standard Test Methods for Particle Size (Sieve Analysis) of Plastic Materials.
21. **ASTM D2338-84(1989)e1** Standard Test Method for Determining Particle Size of Multicolor Lacquers.
22. **ASTM D2862-92** Standard Test Method for Particle Size Distribution of Granular Activated Carbon.

23. **ASTM D2977-71(1996)** Standard Test Method for Particle Size Range of Peat Materials for Horticultural Purposes.
24. **ASTM D3360-96** Standard Test Method for Particle Size Distribution by Hydrometer of the Common White Extender Pigments.
25. **ASTM D4438-85** Standard Test Method for Particle Size Distribution of Catalytic Material by Electronic Counting.
26. **ASTM D4464-85** Standard Test Method for Particle Size Distribution of Catalytic Material by Laser Light Scattering.
27. **ASTM D4513-97** Standard Test Method for Particle Size Distribution of Catalytic Materials by Sieving.

28. **American Society for Testing Materials (ASTM). "Practice D3974-81(1999) Standard Practices for Extraction of Trace Elements from Sediments." Annual Book of Standards, Vol. 11.02, (2001).**

    Procedures partial extraction of soils, bottom sediments, suspended sediments, and waterborne materials to determine the extractable concentrations of certain trace elements including aluminum, cadmium, chromium, cobalt, copper, iron, lead, manganese, nickel, and zinc.
    Keywords: heavy metals, methodology, solid fraction.

29. **American Society for Testing Materials (ASTM). "Practice D3976-92(1996) Standard Practice for Preparation of Sediment Samples for Chemical Analysis." Annual Book of Standards, Vol. 11.02, (2001).**

    Standard procedures for preparation of test samples of field samples collected from locations such as streams, rivers, ponds, lakes, and oceans.
    Keywords: heavy metals, methodology, solid fraction

30. **American Society for Testing Materials (ASTM). "Practice D4698-92(1996) Standard Practice for Total Digestion of Sediment Samples for Chemical Analysis of Various Metals." Annual Book of Standards, Vol. 11.02, (2001).**

    Two procedures for the total digestion of sediments for subsequent determination of metals by atomic absorption spectrometer (AAS) or inductively coupled plasma (ICP) analysis are presented.
    Keywords: heavy metals, methodology, solid fraction

31. **American Society for Testing Materials (ASTM). "Practice D5369-93(1998) Standard Practice for Extraction of Solid Waste Samples for Chemical Analysis Using Soxhlet Extraction." Annual Book of Standards, Vol. 11.04, (2001).**

    Procedures for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sediments, sludges, and granular wastes using Soxhlet extraction. Extracts are suitable for analysis by various techniques such as gas chromatography with flame ionization detection (GC/FID) or gas chromatography with mass spectrometric detection (GC/MS). This procedure is recommended only for solid samples that can pass through a 10-mesh sieve (~2-mm).!
    Keywords: organics, methodology, solid fraction, extraction!

32. **American Society for Testing Materials (ASTM). "Practice D6010-96 Standard Practice for Closed Vessel Microwave Solvent Extraction of Organic Compounds from Solid Matrices."** <u>Annual Book of Standards,</u> **Vol. 11.04, (2001).**

Closed vessel microwave extraction of sediments for subsequent determination of solvent extractable semivolatile and nonvolatile organic compounds by such techniques as gas chromatography and gas chromatography-mass spectrometry. This procedure is recommended only for solid samples that can pass through a 10-mesh sieve (~2-mm). For these methods to be applicable, the extraction solvent must have a boiling point less than that of water at ambient pressure. The total solvent extractable content (TSEC) of a sediment waste depends upon the solvent and method used for the extraction procedure.
<u>Keywords:</u> organics, methodology, solid fraction, extraction

33. **American Society for Testing Materials (ASTM). "Test Method D5368-93 Standard Test Methods for Gravimetric Determination of Total Solvent Extractable Content (TSEC) of Solid Waste Samples."** <u>Annual Book of Standards,</u> **Vol. 11.04, (2001).**

Standard procedures for gravimetrically determining the total nonvolatile and semi-volatile organic content of solvent extracts from soils or solid wastes. These methods are used after a solvent extract is obtained from sediment. For these methods to be applicable, the extraction solvent must have a boiling point less than that of water at ambient pressure. The total solvent extractable content (TSEC) of a sediment waste depends upon the solvent and method used for the extraction procedure.
<u>Keywords:</u> organics, methodology, solid fraction, extraction!!

34. **American Society for Testing Materials (ASTM)."Practice D1971-95 Standard Practices for Digestion of Samples for Determination of Metals by Flame Atomic Absorption or Plasma Emission Spectroscopy."** <u>Annual Book of Standards,</u> **Vol. 11.01, (2001).**

Digestion procedures whereby metals associated with the solid fraction of a sample can be brought into solution for subsequent atomic absorption spectrometer (AAS) or inductively coupled plasma (ICP) analysis.
<u>Keywords:</u> heavy metals, methodology, dissolved fraction **ASTM D4570-86(1993)e1** Standard Test Method for Rubber Chemicals-Determination of Particle Size of Sulfur by Sieving (Dry).

35. **ASTM D4822-88(1994)e1** Standard Guide for Selection of Methods of Particle Size Analysis of Fluvial Sediments (Manual Methods).
36. **ASTM D502-89(1995)e1** Standard Test Method for Particle Size of Soaps and Other Detergents.
37. **ASTM D5158-93** Standard Test Method for Determination of the Particle Size of Powdered Activated Carbon.
38. **ASTM D5519-94** Standard Test Method for Particle Size Analysis of Natural and Man-Made Riprap Materials.

39. **ASTM D5644-96** Standard Test Method for Rubber Compounding Materials-Determination of Particle Size Distribution of Vulcanized Particulate Rubber.
40. **ASTM D5861-95** Standard Guide for Significance of Particle Size Measurements of Coating Powders.
41. **ASTM E1037-84(1996)e1** Standard Test Method for Measuring Particle Size Distribution of RDF-5.
42. **ASTM E1617-97** Standard Practice for Reporting Particle Size Characterization Data.
43. **ASTM E1772-95** Standard Test Method for Particle Size Distribution of Chromatography Media by Electric Sensing Zone Technique.
44. **ASTM E276-93** Standard Test Method for Particle Size or Screen Analysis at No. 4 (4.75-mm) Sieve and Finer for Metal-Bearing Ores and Related Materials.
45. **ASTM E389-93(1998)** Standard Test Method for Particle Size or Screen Analysis at No. 4 (4.75-mm) Sieve and Coarser for Metal-Bearing Ores and Related Materials.
46. **ASTM E726-96** Standard Test Method for Particle Size Distribution of Granular Carriers and Granular Pesticides.
47. **ASTM F1632-95** Standard Test Method for Particle Size Analysis and Sand Shape Grading of Golf Course Putting Green and Sports Field Rootzone Mixes.
48. **ASTM F577-83(1993)e1** Standard Test Method for Particle Size Measurement of Dry Toners.
49. **ASTM F660-83(1993)** Standard Practice for Comparing Particle Size in the Use of Alternative Types of Particle Counters.
50. **ASTM F751-83(1993)e1** Standard Test Method for Measuring Particle Size of Wide-Size Range Dry Toners.

51. **Bay, S,M., D.J. Greenstein, S.-L. Lau, M.K. Stenstrom, C.G. Kelley. "Toxicity of dry weather flow from the Santa Monica Bay watershed." Bulletin of the Southern California Academy of Sciences, vol. 95, 33-45, (1996).**
Grab samples of dry weather flow were collected from Ballona Creek and three other storm drains discharging into Santa Monica Bay. The samples were tested for toxicity using three marine toxicity test methods: purple sea urchin fertilization, giant kelp spore germination and growth, and red abalone embryo development. One to three samples were collected on different dates in 1992 from each of the sites. Toxicity was detected in at least one sample from each of the four locations. The magnitude and frequency of toxicity was greatest at the Ashland Ave. site, which was a sump where water collected and was stagnant for a period of time before discharge. The NOEC for Ashland samples was <5.6% to 18% for all test species. Toxicity was also frequently observed in samples from Ballona Creek. Chemical analysis showed that the Ashland samples contained approximately three-fold higher concentrations of COD (252 mg/L) and DOC (34 mg/L), and approximately one-fourth of the dissolved oxygen concentration (1.6 mg/L), when compared to storm drain samples from the other locations. Toxicity characterization tests of two Ballona Creek samples yielded variable results, indicating that the causative factors may have been different between the samples. Toxicity in the first sample appeared to be due to oxidizing agents, while metals were identified as the most likely toxicant in the second sample.

Stormwater Treatment Implications: Dry weather flow from multiple urban locations is toxic to marine species. The cause of the toxicity is variable and includes metals and oxidants. Stagnation of runoff collected in sumps may increase the level of toxicity, possibly through the release of toxic metabolites by microorganisms.

52. Buckler, D.R., G.E. Granato. "Assessing biological effects from highway-runoff constituents." U.S. Geological Survey, Northborough, MA. 46 p.,(1999).

This document reviews the various methodologies for assessing the biological effects of contaminants, with an emphasis on applicability to studies of highway runoff. Published reports on the effects of highway runoff were reviewed to investigate: (1) the suitability of existing data for a quantitative national synthesis, (2) the methods available to study the ecological effects of highway runoff, (3) contaminants of concern, and (4) the potential for adverse effects on the roadside environment and receiving waters. Highway runoff and other sources of contamination have the potential to produce adverse effects at many levels of biological organization. Biological effects research encompasses hundreds of different techniques and endpoints, including biochemical/physiological techniques (e.g. enzyme activity, tissue residue analysis, and histopathology), whole organism studies (e.g. fish/invertebrate/plant growth, survival, and reproduction), and population/community studies (e.g. species abundance, index of biotic integrity). Each of these methods has different strengths and weaknesses, as summarized below:!

Biological Assessment Category	Relative cost	Relative sensitivity	Chemical sensitivity	Ecological relevance	Regulatory utility
Biochemical/physiological	Low	High	High	Low	Low
Whole organism	Medium	Medium	Medium	Medium	High
Population/community	High	Low	Low	High	Medium

Because of the diversity of methods and high variability in method documentation, quality assurance, and site description, it is not possible at this time to conduct a national synthesis of highway runoff biological effects data. A review of published reports indicated, however, that highway runoff rarely produces acute effects in laboratory test organisms. Field studies have measured contaminant accumulation in sediments and tissues and observed changes in species abundance and community structure in areas near highway discharges, however. The runoff constituents of potential biological concern that have been identified in these studies include deicing chemicals, metals (including exotic metals associated with automotive components such as antimony, platinum group elements, and rhodium), volatile and semivolatile organics (e.g., PAHs), major ions (e.g., Ca, Na, chlorides, carbonates), oxygen demand/deficit, and sediment. Runoff particulates may produce biological effects through two mechanisms: physical interference and as a source of bioavailable contamination. Biological effects have been observed to occur as the result of sediment releases from highway construction activities. Determination of the

magnitude and cause of effects from highway runoff is complicated by the covariance of habitat and chemical factors, as well as methodological variations (e.g., filtration of the sample or addition of chelating reagents to algal test media). A battery of test species and methods are recommended by some scientists to assess the biological effects of highway runoff.

Keywords: Stormwater, highway runoff, toxicity, bioaccumulation, literature review, benthic community, receiving water, suspended particles.

Stormwater Treatment Implications: Biological effects of highway runoff are caused by many different constituents, which can be present in either the dissolved phase or sorbed to particulates. Adverse impacts to benthic communities in streams and other receiving waters are caused by highway runoff. A battery of biological tests are needed to adequately characterize the extent of biological impacts of stormwater.

53. **Breault, R.F., and Granato, G.E. "A Synopsis of Technical Issues of Concern for Monitoring trace Elements in Highway and Urban Runoff." U.S. Geological Survey Open File Report 00-422, 67 p.**

The purpose of this report is to examine the technical issues associated with the monitoring of the trace element chemistry of highway and urban runoff, to discuss trace element monitoring artifacts, and to discuss matrixes of potential use for monitoring trace elements. The primary focus of the report is the sampling of trace elements in storm water flow-specific all, runoff on the pavement, in drainage structures, structural BMPs, and discharges to receiving waters.

Keywords: highway runoff, urban runoff, heavy metals, monitoring, BMPs

54. **Beckett, R., Murphy, D., Tadjiki, S., Chittleborough, D.J., Giddings, J.C.!!"Determination of Thickness, Aspect Ratio and Size Distributions for Platey Particles Using Sedimentation Field-Flow Fractionation and Electron Microscopy." Colloids and Surfaces A – Physiochemical and Engineering Aspects, 120(1-3), 17-26, (1997).**

Sedimentation field-flow fractionation (SdFFF) is used to prepare fractions of very narrow mass range for electron microscopic (EM) analysis. By assuming equal particle density for all particles within a specified size fraction the equivalent spherical diameter for the particles can be calculated from SdFFF theory. From micrograph images of each particle, used in conjunction with the equivalent spherical particle diameter (from SdFFF) the particle thickness and aspect ratio is calculated. Thus SdFFF-SEM provides a semi-quantitative measure of clay morphology across the particle size distribution of the sample. Three clay minerals were examined: Purvis School Mine, RM30, and Muloorina illite (Clay Society).

Keywords: Aspect ratio, clays; electron microscopy, sedimentation field-flow fractionation; size distribution, thickness

Stormwater Treatment Implications: Demonstrate fractionation of standard clay particles for subsequent identification using electron microscopy. Somewhat useful for laboratory analysis. Not suitable for field deployment.

55. **Blo,G., G., Contado, C., Fagioli, F., Dondi, F. "Size—Elemental Characterization of Suspended Particle Matter by Split-Flow Thin Cell**

Fractionation and Slurry Analysis—Electrothermal Atomic Absorption Spectrometry." Analyst, 125(7), 1335 - 1339!, (2000).

Suspended particle matter from natural waters is characterized by combining split-flow thin (SPLITT) cell separation and elemental spectroscopic identification. Results are reported for the determination of Al and Fe in mineral particulates. The developed procedure was applied to a sample from the Po river, where trace elements of environmental interest were determined for the whole fraction in the 0.2—25 µm dimensional range as well as for some sub-fractions obtained by SPLITT fractionation. A 50L sample was filtered through a Whatman 542 filter paper (nom. Pore size 20-25 µm) and the filtrate was concentrated (200:1) by tangential filtration through a 0.2 µm Durapore membrane filter in a Minitan apparatus (Millepore). The concentrated slurry was 6180 mg/L, in the 0.2-20 µm range.

Keywords: split-flow thin cell fractionation, particle matter analysis, natural sediments.

Stormwater Treatment Implications: Laboratory technique for size fractionation of environmental samples. Not suitable for field deployment.

56. **Burba,P., Aster, B., Nifant'eva, T., Shkinev, V., Spivakov, B. Ya. "Membrane Filtration Studies of Aquatic Humic Substances and their Metal Species: a Concise Overview, Part 1. Analytical Fractionation by Means of Sequential-Stage Ultrafiltration."Talanta, 45, 977-988, (1998).**

Fractionation of aquatic humic substances using sequential-stage ultrafiltration (UF) is discussed with emphasis on on-line techniques. UF's application with respect to size classification in colloidal aquatic systems is considered relative to i) reliability and quality of the applied membranes (e.g. their pore size classification and calibration), ii) polarization (or coagulation) of the colloids on the membrane surface, iii) undesired sorption on polymer surfaces, and iv) low throughput for membranes with low NMWCO (<5 kDa) and small surface area. Size classification using UF is strongly dependent on operation parameters. Disadvantages are overcome by prefiltration using microfiltration (MF) and cascade arrangement of high-performance UF membranes which also allows on-line, continuous flow, operation. Combination of MF-UF appears promising for the size classification of natural water samples not altered by any reagents, buffers or electrolytes. By combining EDTA exchange with MF-UF, the lability of natural HS/metal species can be differentiated as a function of their molecular size. Results not verified by size analysis.

Keywords: Environmental samples, fractionation, sequential-stage ultrafiltration.

Stormwater Treatment Implications: Technique for size fractionation of slurry samples. Possible field deployment. Size fractionation efficiency not demonstrated.

57. **Beckett, R., Murphy, D., Tadjiki, S., Chittleborough, D.J., Giddings, J.C.!!"Determination of Thickness, Aspect Ratio and Size Distributions for Platey Particles Using Sedimentation Field-Flow Fractionation and Electron Microscopy."Colloids and Surfaces A – Physiochemical and Engineering Aspects, 120(1-3), 17-26, (1997).**

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Keywords: Aspect ratio, clays; electron microscopy, sedimentation field-flow fractionation; size distribution, thickness
Stormwater Treatment Implications: Demonstrate fractionation of standard clay particles for subsequent identification using electron microscopy. Somewhat useful for laboratory analysis. Not suitable for field deployment.

58. **Blo,G., G., Contado, C., Fagioli, F., Dondi, F. "Size—Elemental Characterization of Suspended Particle Matter by Split-Flow Thin Cell Fractionation and Slurry Analysis—Electrothermal Atomic Absorption Spectrometry". Analyst, 125(7), 1335 - 1339, (2000).**

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Keywords: split-flow thin cell fractionation, particle matter analysis, natural sediments.
Stormwater Treatment Implications: Laboratory technique for size fractionation of environmental samples. Not suitable for field deployment.

59. **Burba,P., Aster, B., Nifant'eva, T., Shkinev, V., Spivakov, B. Ya. "Membrane Filtration Studies of Aquatic Humic Substances and their Metal Species: a Concise Overview, Part 1. Analytical Fractionation by Means of Sequential-Stage Ultrafiltration". Talanta, 45, 977-988, (1998).**

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<u>Keywords</u>: Environmental samples, fractionation, sequential-stage ultrafiltration.

<u>Stormwater Treatment Implications</u>: Technique for size fractionation of slurry samples. Possible field deployment. Size fractionation efficiency not demonstrated.

60. Caldwell, K.D. "Field-Flow Fractionation." Analytical Chemistry, 60(17), 959A-971A, (1988).

Overview of field-flow fractionation (FFF) techniques using different field-induced equilibrium zones for directed partitioning. The channel is generally a thin duct with height around 250 μm thick and width to height ration larger than 50. Size range of FFF is between 5×10^{-9} m and 50×10^{-6} m. Retention is controlled by external fields and gradients: flow, gravitational, thermal, steric, electrical. The availability of theoretical models that describes retention and zone broadening for different FFF field types simplifies prediction of fractionation efficiencies. Sample sizes usually in the 1 mL to 5 mL range.

<u>Keywords</u>: field-flow fractionation, fields, particle matter analysis.

<u>Stormwater Treatment Implications</u>: Laboratory technique for fractionation of particle laden aqueous samples. Detection systems and instrument calibration not discussed. Not suitable for field deployment.

61. Cao, W., Williams,P.S., Marcus N. Myers, M.N., and Giddings, J.C. "Thermal Field-Flow Fractionation Universal Calibration: Extension for Consideration of Variation of Cold Wall Temperature." Analytical Chemistry. 71 (8), 1597 -1609, (1999).

A calibration method has been proposed for thermal field-flow fractionation (ThFFF) where the calibration constants closely describe the ratio of ordinary (molecular) diffusion coefficient D to thermal diffusion coefficient (thermophoretic mobility) D_T. Systematic experiments have been carried out to verify this calibration method for a wide range of conditions. This paper quantifies the effect of cold wall temperature on polymer retention in ThFFF.

<u>Keywords</u>: Thermal field-flow fractionation, calibration.

<u>Stormwater Treatment Implications</u>: Report focuses on calibration of thermal field-flow-fractionation for polymers fractionation. Not useful for laboratory analysis of particles. Not suitable for field deployment.

62. Chittleborough, D.J., Hotchin, D.M., Beckett, R. "Sedimentation Field-Flow Fractionation: A New technique for the Fractionation of Soil Colloids." Soil Science, 153(5), 341-348, (1992).

Application of sedimentation field-flow fractionation (SdFFF) of soil colloids of submicron size up to $5x10^{-7}$ m is described. In the case of SdFFF a centrifugal field is applied across the thin dimension of the channel causing particles to migrate toward the outer wall. At the same time particles diffuse in the opposite direction as a result of Brownian motion. After a certain relaxation time has elapsed, an equilibrium concentration distribution of each particulate species is established near the wall. Channel flow is then commenced and the parabolic velocity distribution profile will sweep out the particles with the largest diffusion coefficient first. Particles with low mass are eluted first followed by heavier particles. Fractions were generated in much shorter time than standard fractionation methods such as centrifugation in a continuous action rotor.
Keywords: sedimentation field-flow fractionation, centrifugal field.
Stormwater Treatment Implications: Demonstrates application of sedimentation field-flow-fractionation for soil colloids. The main disadvantage for clay mineral studies is that the small mass of each size fraction obtained limits the analysis of size fractions by X-ray diffraction. Useful for laboratory analysis. Not suitable for field deployment.

63. Contado, C., Dondi, F., Beckett, R., Giddings, J.C.!!"Separation of Particulate Environmental Samples by SPLITT Fractionation Using Different Operating Modes."Analytica Chimica Acta, 345(1-3), 99-110, (1997).

Procedures for preseparation of particle suspensions prior to sedimentation field flow fractionation (SdFFF) analysis based on the use of split-flow thin cell (SPLITT) fractionation, were examined for isolating size fractions from both polydisperse standard silica samples and natural river particle samples. Two modes of SPLITT cell operation are compared. Recycling procedures for enhancing the resolution were tested. Degree of the separation attained was checked by optical microscopy and scanning electron microscopy (SEM) of the fractionated samples. The advantage is that no external dilution is introduced during splitting maintaining chemical composition and sample concentration.
Keywords: SPLITT fractionation; Silica particles; River borne particles; Size separation
Stormwater Treatment Implications: Demonstrates fractionation of river water colloids. Potentially very useful for laboratory analysis. Not suitable for field deployment.

64. Characklis, G.W. and M.R.,Wiesner. "Particles, metals, and water quality in runoff from large urban watershed." ASCE J. of Environmental Engineering, vol. 123(8), 753-759, (1997).

Water samples were collected under storm and non-storm conditions from five sites along the Brays and Keebans Bayous in Houston, TX. Zn and TOC were present primarily in the dissolved fraction (<0.45 μm) under non-storm conditions; the concentration of these two contaminants in the macrocolloidal fraction (>0.45 μm)

increased significantly during storms. In contrast, Fe and suspended solids were present primarily in the macrocolloidal fraction under both storm and non-storm conditions. The Zn/TOC and Fe/SS couples were eluted at different points of the storm hydrograph; specifically, the peak concentrations of Zn/TOC coincided with peak flow, while the peak concentrations of Fe/SS occurred later. No "first flush" effect was observed, which was attributed to the integrated effect of many small watersheds contributing to the pollutant loads observed at the Brays and Keebans Bayous. The PSDs present in storm water flow evolve over the course of a storm; specifically, the number of particles <2.5 μm in size first increase and then decrease during the course of a storm. Protocols are described for measuring pollutants in the two different particle size fractions.

Keywords: Particle size, Water pollution, Urban watershed, Metals, Occurrence

Stormwater Treatment Implications: This study found that there was no first flush effect for the pollutant loads from a large (240 km^2) watershed. The authors calculate that in order to treat 60% of the pollutant load from this entire watershed, 50% of the storm flow would need to be diverted. The authors conclude that it may be more feasible to treat runoff flowing out of smaller sub-watersheds because pollutant loads from such systems are more likely to exhibit first flush behavior. However, design of such treatment systems will be difficult, because different pollutants are located in different portions of the PSD (e.g., Zn is dissolved, Fe is particulate), and the Zn/TOC and Fe/SS couples may require separate treatment strategies.

65. **Chebbo, G., A. Bachoc. "Characterization of suspended solids in Urban Wet Weather Discharges." Water Sci. Technol., 25(8), 171-9, (1992).**

Storm water samples were collected from several storm sewers and combined sewer systems in Paris, France, and analyzed for pollutants, and characterized relative to particle size, mass and settling velocity. Particle-associated pollutants were a significant percentage of the total pollutant levels measured in all samples: COD (84-92%), BOD5 (77-91%), TKN (57-82%), hydrocarbons (86-99%), and Pb (79-100%). Fine particles (24-45 μm diameter) were most numerous. Particles smaller than 100 microns had higher specific gravity (2.5) compared to particles greater than 100 microns (1.8); this difference apparently reflects a higher organic content for the larger particles. The measured settling velocities of the fine particles (25 to 44 μm) were large (4 to 10 m/h) compared to velocities predicted by Stokes' law for equivalent spheres; however, the measured velocities were only 3 to 4 times greater than Stokes' law prediction, compared to 1000 fold difference reported by other researchers.

Keywords: Urban runoff pollution; separate storm discharges; combined sewer overflows; particulate pollutants; stormwater solids sampling; particle size; specific mass; settling velocity ; sedimentation.

Stormwater Treatment Implications: Authors conclude that particle settling will be a very efficient treatment scheme because most of the pollutants are associated with fine particles that have high specific gravity and fast settling rates. Authors suggest that treatment options that facilitate settling of particles (e.g., settling basins, slow flows) will lead to an improvement in storm water quality.

66. Chebbo, G., P. Musquere, V. Milisic and A. Bachoc. "Characterization of solids transferred into sewer trunks during wet weather." <u>Water Science and Technology</u>**, vol. 22(10/11), 231-238, (1990).**

This paper presents the results of study of storm sewers in Bordeaux, France. The data suggest that suspended 10-20 micron particles are the significant vectors of pollution during storms.
<u>Keywords:</u> Stormwater solids, stormwater pollution, particle size, particle settling velocity, particle density, stormwater sampling.
<u>Stormwater Treatment Implications:</u> Because most of the contaminants in storm sewers are associated with suspended particles, sedimentation basins may be an effective pollution management tool.

67. Chui P.C."Characteristic of Stormwater quality from Two Urban Watersheds in Singapore."Environmental Monitoring and Assessment, 44(1-3):173-181, (1997 Feb.).

This paper presents the results of a study on the quality of storm water runoff from two adjacent urban watersheds in Singapore. The water samples collected were analyzed for physical and chemical constituents. The ranges and mean concentrations of common water quality parameters were established, and the loading histories of selected parameters were studied.
<u>Keywords:</u> storm water, water quality, urban runoff, pollutants
<u>Stormwater Treatment Implications:</u> Treatment of the first flush may be an effective way to remove pollutants in stormwater runoff.

68. Crabtree, R.W. "Sediments in Sewers." J.IWEM, vol. 3, 569-576, (1989).

This paper was motivated by the observation that up to 90% of the pollution discharged from storm sewage overflows (SSOs) is derived from the erosion of in-pipe sediment and silt. The author presents a classification system for sediments in sewer systems, and then presents data on the physical characteristics and pollutant loads associated with each class. The proposed classification is as follows: Type A are coarse, loose, granular, predominantly mineral, material found in the inverts of pipes; Type B are as A, but cemented by the addition of fat, bitumen, cement, etc. into a solid mass; Type C are mobile, fine grained deposits found in slack flow zones, either in solution or above Type A material; Type D is organic pipe wall slimes and zoogloeal biofilms around the mean flow level; Type E are fine grained mineral and organic deposits found in storm sewer overflow storage tanks. Type D deposits contain the highest concentrations (on a dry weight basis) of COD, BOD4, organic content, and fats/oil/grease. However, when taking into account the abundance of each sediment type in a typical sewer pipe, the author argues that Types C and A deposits will contribute most to the pollutant loading from SSOs during storms. Author also reports on the critical yield stresses needed to mobilize different deposits, and all sediment types are found to be highly resistant to erosion.
<u>Keywords:</u> Combined sewer, sediment, overflow, and polluting potential.
<u>Stormwater Treatment Implications:</u> Most of the receiving water impact of storm flows may be due to erosion of in-pipe sediments, not wash-off of pollutants from roadway surfaces. If true, then end-of-pipe treatment schemes or sewer sediment

removal programs may be more effective at mitigating the impact of stormflows than roadside BMPs.

69. **Doherty, F.G., A.A. Qureshi, J.B. Razza. "Comparison of the *Ceriodaphnia dubia* and Microtox inhibition tests for toxicity assessment of industrial and municipal wastewaters." Environmental Toxicology, vol. 14, 375-382,(1999).**

Samples of effluent from manufacturing facilities, wastewater treatment plants, and stormwater were tested with two types of acute toxicity tests: a 24 & 48 hr *Ceriodaphnia dubia* survival test and a 15 minute Microtox luminescence test. A total of 16 samples were tested and agreement among the tests (either toxic or nontoxic) was present for 13 samples. Microtox did not detect toxicity in one sample that was toxic to *C. dubia*, while two other samples that were toxic to Microtox did not affect survival of *C. dubia*. The results indicate that Microtox is a useful test for screening samples for toxicity. Other studies that have compared these two tests have reported less of a correspondence between the methods. Some of these differences are likely due to the lower sensitivity of Microtox to specific chemicals such as diazinon (EC50=18 mg/L), copper, zinc, cadmium, phenol, and pentachlorophenol. Site-specific comparative tests are recommended to determine whether Microtox is an appropriate surrogate toxicity test species for a specific type of effluent.
Keywords: toxicity, effluent, Microtox, water flea
Stormwater Treatment Implications: The Microtox test may be a useful screening tool for runoff toxicity, but comparative tests with other species are needed to determine whether the results for a specific type of effluent are comparable.

70. **Droppo, I.G., Krishnappan, B.G., Rao, S.S. and Ongley, E.D. "Investigation of a Sequential Filtration Technique for Particle Fractionation." Environmental Science and Technology, 29, 2, 546-550, (1995).**

Sequential filtration for particle fractionation was investigated using a fully dispersed inorganic bottom sediment from Lake Eire (Port Stanley/Port Burwell area). The sediment was wet sieved using 62 um mesh and the smaller fraction used for the fractionation experiment. A total of 0.75 g of sediment was suspended in 300 mL of 10% solution of sodium hexametaphosphate — approximate concentration of 2500 mg/L. The sample was then subdivided into three sub-samples by pipeting. The sequential filtration procedure consisted of passing the sub-sample once through a series of filters arranged in descending orders of filter pore sizes: 60, 41, 20, 10 μm (Nitex nylon monofilament screening fabric filters), and 8 μm (Nuclepore polycarbonate membrane filter). After fractionation 19% of weight was unaccounted for size fractionation. But this approach was considered very inaccurate as filters retained a wide distribution of sizes both smaller and larger than the targeted size classes. Particle size determination was performed by Malvern near-forward-Fraunhofer diffraction spectrum. Limitations of size analysis was not discussed.
Keywords: Environmental samples, fractionation, sequential-stage filtration, light diffraction.
Stormwater Treatment Implications: Technique for size fractionation of particulate samples. Not suitable for field deployment. Not recommended for laboratory use.

71. Davis, E.M., D.M. Casserly, J.D. Moore. "Bacterial relationships in stormwaters." Water Resources Bulletin,Vol. 13, No. 5, 895-905,(1977).

Concentrations of indicator bacteria in stormwater runoff was monitored for a three-year period in a developing rural area approximately 30 miles north of Houston, Texas. Bacteria pollutographs exhibited first flush behavior; fecal streptococci (or enterococci bacteria) may be the most useful bacterial group in determining stormwater quality. Nearly all samples required 8 mg/L to 16 mg/L chlorine, or an excess of 32 mg/L of ozone, for disinfection.
Keywords: Coliform; storm water disinfection; urbanization; land use; water quality
Stormwater Treatment Implications: Provides data on the disinfectant concentrations needed to remove indicator bacteria from stormflows.

72. Davis, J.B, J.J. George. "Benthic invertebrates as indicators of urban and motorway discharges." The Science of the Total Environment, vol. 59, 291-302, (1987).

The use of biota to monitor water quality was investigated at 5 different locations along a tributary or the river Thames in England. pH ranged from 7.2-8.8, alkalinity 73-215 mg/L $CaCO_3$, DO 88.4-104.2 % saturation, BOD 3.8-6.7 mg/L, SS 11.0-22.0 mg/L, Ammonia Nitrogen 0.3-0.6 mg/L, Nitrate Nitrogen 6.6-9.9 mg/L, Cu 0.014-0.020 mg/L, Mn 0.025-0.042 mg/L, Zn 0.025-0.046 mg/L, Pb 0.029-0.049 mg/L. It was found that the structure and composition of the invertebrate community is affected by organic enrichment Analysis of the invertebrate tissue appears to be a useful tool for detecting low level metal contamination.
Keywords: Invertebrate, Roadway, Urban runoff
Stormwater Treatment Implications: Invertebrate tissue sampling could serve as an effective method of monitoring stormwater impacts on receiving waters.

73. Drapper, D., R. Tomlinson, and P. Williams."Pollutant Concentrations in Road Runoff: Southeast Queensland Case Study." Journal of Environmental Engineering, 126(4): 313-320, (2000 April).

Stormwater runoff samples were collected from 21 highway sites in southeast Queensland, Australia. The runoff samples were tested for a number of heavy metals, hydrocarbons, pesticides, and other physical characteristics. Traffic volume is found to be a poor indicator of road runoff pollutant concentrations. Inter-event duration is found to be a statistically significant factor for pollutant concentrations.
Keywords: pollutant, highway runoff, particle size distribution, heavy metals, PAHs, pollutant loads
Stormwater Treatment Implications: Inter-event duration, not traffic volumes, is an important predictor of pollutant loads in highway runoff.

74. Driscoll, E.D., P.E. Shelley and E.W. Strecker. "Pollutant loadings and impacts from highway runoff, Volume III: Analytical investigation and research reports." FHWA-RD-88-008. FHWA, U.S. Department of Transportation. 1-139, (1990).

The primary purpose of this study was to develop a procedure for predicting the quantity of, and pollutant levels in, highway stormwater discharges. Study assembles

and analysis water quality monitoring data from 993 separate storm events at 31 highway runoff sites distributed among 11 states, and considers source characteristics and mechanisms involved in the generation of highway runoff pollutants. Secondary objectives of the study were: (1) to develop procedures for using pollutant discharge estimates and local site conditions to determine whether highway runoff will cause receiving water quality impairment, and (2) to describe procedures for identifying appropriate BMPs.
Keywords: Highway Runoff, Water Pollution, Nonpoint source, Stormwater Loads, Water Quality
Stormwater Treatment Implications: Describes a procedure for selecting stormwater BMPs based on water quality data base and predictive modeling.

75. **Edwards, T.K. and G.D. Glysson. "Field methods for measurement of fluvial sediment: U.S. Geological Survey Techniques of Water-Resources investigations."(1999).**

This report describes equipment and procedures for collection and measurement of fluvial sediment. A discussion of the basic concepts involved in the processes of erosion, transport, and deposition sediment sampling equipment and procedures necessary to representatively sample and measure fluvial sediments.
Keywords: Fluvial, sediments, bed-load, erosion, transport, deposition.

76. **Ellis, B. "Urban Runoff quality in the UK: Problems, Prospects and Procedures." Applied Geography, 11(3):187-200,(1991 July).**

A review of the impacts of urban runoff on receiving water quality in the UK. Pollution sources, stormwater transport, and impact on receiving water impacts are described.
Keywords: urban runoff, pollutants, biological impact.
Stormwater treatment implications: Treating runoff only during certain phases of a storm may be a cost-effective way of reducing the impact of runoff on receiving water quality.

77. **Ellis, J.B., D.M. Revitt, and N. Liewellyn. "Transport and Environment: Effects of Organic Pollutants on Water Quality." Journal of the Chartered Institution of Water and Environment Management,11(3):170-177,(1997).**

This paper identifies the magnitude and extent of pollution associated with discharges from various highway sources and identifies metals, hydrocarbons, herbicides and deicing agents as the principle contaminants of environmental concern. The impacts of these pollutants on the receiving water are reviewed.
Keyword: highway runoff, organics, water quality
Stormwater Treatment Implications: A stormwater treatment strategy must include a plan to treat pollutants that can be transported from a multitude of local sources.!!

78. **Ellis J. B. and D. O. Harrop. "Variations in solids loadings to roadside gully-pots." The Science of the Total Environment, vol. 33, 203-311, (1984).**

Presents data on the composition of road surface particulates that flow into roadside gully pots near a housing estate near Metropolitan London. Solids discharged to the

gully pots had median particle size of 600 to 1000 μm; two-thirds of the particles were between 400 and 3000 μm, about 10% of the particle mass was less than 400 μm, and 5% of the mass was less than 60 μm. Seasonal fluctuations in runoff sediment loadings were observed due to variations in rainfall and runoff volumes.
Keywords: gully pots, rainfall, particles, street sediments
Stormwater Treatment Implications: Treatment BMPs should focus be designed to treat the portion of the particle size distribution that contains the most contaminants.

79. Ellis, B.J., D.O. Harrop, D. M. Revitt. "Hydrological controls of pollutant removal from highway surfaces."Water Res., 20(5), 589-95, (1986).

Presents a stepwise linear regression analysis of pollutant loadings against the following hydrological parameters: total rainfall volume, maximum 5 minute duration rainfall intensity, storm duration, antecedent dry period length, total surface discharge. It was found that the general trend of heavy metal concentrations were Fe>Mn>Pb>Zn>Cu>Cd, and the magnitude of pollutant loadings are primarily controlled by storm flow and duration; the antecedent dry period seems to be a negligible factor.
Keywords: sediment loadings, heavy metal loadings, rainfall-runoff losses, hydrological parameters, stepwise linear regression analysis, pollutant removal rates, gully-pots (catch basins).
Stormwater Treatment Implications: Analysis of input and removal rates suggested that aerial deposition may be a primary source of metals in stormwater sewers. Therefore regulation of these metals in the atmosphere maybe an efficient BMP for lowering stormwater toxicity.

80. Ellis, J.B., D.M. Revitt. "Incidence of heavy metals in street surface sediments: solubility and grain size studies." Water, Air, and Soil Pollution, vol. 17, 87-100, (1982).

Dry sediments were collected from pavement and gutters at a number of road sites in N.W. London during July 1979 after an antecedent dry period of several weeks. The samples were sized by dry/wet sieving and standard pipette procedures. The particle size distributions of Pb, Cd, Zn, Mn, Fe, and Cu are represented as cumulative probability plots. Metal size distribution plots were generated for several different sites including: a gutter alongside a major highway (maximum 4000 vehicles/h), from the gutter of a moderately busy highway (maximum 1750 vehicles/h), from the gutter of a residential side street, and from the edge of a rural road. Authors claim that the similarity of the Mn and Fe size distribution across all sites implies that the observed concentrations represent natural background levels. For busy highways, Cd and Pb are enriched between 100 and 500 microns, and it is proposed that these metals are associated with particle aggregates. Cd, Fe, and Zn are enriched in the coarsest grain fractions along residential side streets. The leaching of metals from roadway sediments was independent of road type and followed the order: Cd>Zn, Cu>Mn>Pb. Zn and Cu went into solution very quickly, indicating that these metals might be rapidly mobilized into storm flow during first flush. Authors point out that the kinetics of metal release from roadway sediments could be an important factor in receiving water impacts.

Keywords: Traffic densities, sedimentation, extraction efficiency, leachate.

Stormwater Treatment Implications: The distribution of metals among particle sizes follows a nearly log-normal distribution, implying that treatment systems must remove a very large range of particle sizes to affect a complete removal of metals. Metal-to-metal and site-to-site variability is also significant; e.g., Cd is enriched in the small size of the size distribution (10 to 100 microns) at the rural site, but not at the highway site.

81. **Estèbe, A., J.-M. Mouchel, D.R. Thévenot. "Urban runoff impacts on particulate metal concentrations in River Seine." Water, Air, and Soil Pollution, vol.108 (1/2), 83-105, (Nov. 1998).**

Sediment traps were deployed in the river Seine near Paris, and the recovered particles were analyzed for the concentration of Cd (4-9 mg/kg), Cu (200-300 mg/kg), Pb (200-400 mg/kg), and Zn (400-1000 mg/kg). Researchers found that particle-associated metals released into the Seine during storm events quickly settled to the river bottom. These sediments contribute to the chronic metal contamination of the river by a slow re-suspension mechanism.

Keywords: CSO, heavy metal, river, suspended solids, urban runoff.

Stormwater Treatment Implications: The sediment trap design employed here could be used to passively sample particles associated with storm water. Study also demonstrates that metal contamination is associated with suspended particles in storm flows.

82. **Field, R., "Use of coliform as an indicator of pathogens in storm-generated flows." *Proc., 6th Int. Conf. on Urban Storm Drainage*, Ontario, Canada,(1993).**

Review article questions the use of indicator bacteria to characterize the receiving water quality impact and disease-producing potential of stormwaters. Future epidemiological studies that assess the impacts of stormwater on human health should include measurements of both enteric and non-enteric pathogens.

Keywords: Stormwater, Indicators, bacteria, pathogen

Stormwater Treatment Implications: Water quality and disinfection criteria for pathogenic bacteria and viruses are needed for stormwater and combined sewer outlets.

83. **Field, R., M. O'Shea, M.P. Brown. "The Detection and Disinfection of Pathogens in Storm-Generated Flows." Water Science Technology. Vol. 28, No 3-5, 311-315, (1993).**

The human health impact of stormwater flows cannot be assessed using indicator bacteria densities. The authors note that previous epidemiological studies show little correlation between fecal indicator densities from stormwater and swimming related illnesses. Stormwater runoff can have low concentrations of fecal indicator bacteria and high concentrations of non-enteric pathogens such as staphylococcus, *Pseudomonas aeruginosa*, *Klebsiella* and adenoviruses, all of which can be associated with recreational swimmers illnesses. It is argued that all runoff be disinfected by some means before it is allowed to enter recreational receiving waters.

Keywords: Stormwater, disinfection, microorganisms, water-quality indicators.

The treatment of all stormwater maybe necessary to reduce the health risk of stormwater impacted recreational waters.

84. **Field, R., and M.L. O'Shea. "The Handling and Disposal of Residuals from the Treatment of Urban Stormwater Runoff from Separate Storm Drainage Systems." Waste Management and Research 12: 527-539,(1994).**

The wide-spread treatment of stormwater would generate solid residuals in amounts that equal, or exceed, the volume of sludge now generated by municipal wastewater treatment. The characteristics of storm water runoff differ substantially from that of wastewater or combined sewer overflow (CSO) in several important parameters, most notably suspended solids (SS) and organic content.
Keywords: storm water runoff, storm water treatment residuals
Stormwater Treatment Implications: The large volumes of sludge generated by wide-spread treatment of stormwater would require new approaches for treatment and disposal.

85. **Fisher, D.J., M.H. Knott, S.D. Turley, B.S. Turley, L.T. Yonkost, G.P. Ziegler. "The acute whole effluent toxicity of storm water from an international airport." Environmental Toxicology and Chemistry, vol. 14, 1103-1111, (1995).**

Stormwater runoff from two different sites at the Baltimore-Washington International Airport were measured for toxicity using two species of fish, *Pimephales promelas* and the *Daphnia magna*. Water quality parameters were found to vary across storm events relative to DO (8.6-6.7 mg/L), pH (5.91-8.48), conductivity (120-2000 μmho), alkalinity (30-520 mg/L as $CaCO_3$), hardness (28-880 mg/L as $CaCO_3$), total glycol (11-230900 mg/L). The glycol levels in the fish were found to range from 1,753-5,408 mg/L for the *Pimephales promelas* and 2,003-8,666 mg/L for the *Daphnia magna*. Glycols used in deicing mixtures account for the majority of the toxicity in the stormwater runoff.
Keywords: Storm water, Acute toxicity, Deicing mixtures, Freshwater, Airport
Stormwater Treatment Implications: Deicing agents contributes toxicity to stormwater flows.

86. **Folkeson, L. "Environmental Effects of Highway Runoff Water, A Literature Review." VTI Report No. 391A, Swedish National Road and Transport Research Institute, (1994).**

Reviews the transport and ecological effects of highway runoff pollutants in rural environments. Highway runoff water contains suspended solids, oxygen consuming pollutants, nutrients, heavy metals, organic pollutants, and microorganisms.
Keywords: pollutants, highway runoff, heavy metals, PAHs, particulates, contaminant sources
Stormwater Treatment Implications: Summarizes concentration of pollutants measured in runoff from rural highways.

87. Fuchs, S., T. Hairtopoulou, M. Schafer and M. Wilhelmi "Heavy Metals in Freshwater Ecosystems Introduced by Urban Rainwater Runoff Monitoring of Suspended Solids, River Sediments and Biofilms." Water Science and Technology, 36(8-9):277-282,(1997)

Sediments, suspended solids, and biofilm samples at different locations of the Alb River near Karlsruhe, Germany were analyzed for their heavy metal content (Pb, Cu, Cd). The main task of this study was to evaluate the role biofilms play in stormwater pollution by comparing the measured pollution with the results of long term monitoring programs based on sediments and suspended solid samples.
Keywords: heavy metals, pollutants, monitoring, water quality.
Stormwater Treatment Implications: Stormwater treatment strategies should account for the role that biofilms play in stormwater contamination.

88. Fuh, C.B., Myers, M.N., Giddings, J.C. "Analytical SPLITT Fractionation: Rapid Particle Size Analysis and Measurement of Oversized Particles." Analytical Chemistry, 64, 3125-3132, (1992).

Using SPLITT fractionation, particles are separated parallel to the flow by an external field. An outlet splitter separates components with high and low mobilities, directing fractions to different substreams (usually two) for collection and measurement. The method is particularly useful for separation of oversized particles from bulk in process applications. Can be coupled in series for fractionation.
Keywords: SPLITT field-flow fractionation, oversize particles, continuous.
Stormwater Treatment Implications: Demonstrates SPLITT flow field-flow-fractionation for synthetic colloids. Potentially useful for laboratory analysis. Not suitable for field deployment.

89. Garnaud, S., J.-M. Mouchel, G. Chebbo and D. R. Thévenot. "Heavy metal concentrations in dry and wet atmospheric deposits in Paris district: comparison with urban runoff." The Science of the Total Environment, vol. 235(1-3), 235-245, (1 September 1999).

Metal concentrations in atmospheric deposits were compared with stormwater runoff at four sites in and around Paris, France. The percent of Cd, Cu, Pb, and Zn associated with particulates increased in the order: rain, roof, yard/street, and storm outlets. The bulk concentration of metals at all sites ranked as follows: Cd<<Cu<Pb<<Zn. In general, the bulk metal concentration and the fraction of particulate metals increase significantly from rainfall to the sewer outlet, and this effect was much larger at the suburban sites than in the city center.
Keywords: Trace metals, atmospheric deposit, fallout, rain, dissolved/particulate partitioning, urban catchment.
Stormwater Treatment Implications: The bulk metal concentration in storm water runoff is associated with particulate material.

90. Gjessing, E., E. Lygren, S. Anderson, L. Berglind, G. Carlberg, H. Efraimsen, T. Kallqvist, and K. Marinsen. "Acute Toxicity and Chemical Characteristics of Moderately Polluted Runoff from Highways." The Science of the Total Environment, 15(33), (1984).

Runoff from the highway has been characterized by physical, chemical and biological methods. Several organic micro pollutants have been identified, such as PAH's, PCB, and other chlorinated constituents. The biological methods include toxicity tests on salmon, alga, bacteria, and fungi. Studies on the hatching of salmon eggs in the particulate part of the highway runoff are also included. The results suggest an essential part of the potentially toxic organic (and inorganic) pollutants are strongly adsorbed to the particulate matter, and that the acute toxicity of the runoff water to the aquatic organisms studied is moderate.
<u>Keywords:</u> highway runoff, toxicity, PAHs, particulates
<u>Stormwater Treatment Implications</u>: Toxicity is associated with the particulate fraction in highway runoff. Hence, BMP design should consider the role that particulates play in the environmental transport of toxic contaminants.

91. Guerard, P.V., and W. B. Weiss. "Water Quality of Storm Runoff and Comparison of Procedures for Estimating Storm-Runoff Loads Volume, Event Mean Concentrations, and the Mean Load for a Storm for Selected Properties and Constituents for Colorado Springs, Southeastern Colorado 1992." Water Resources Investigations Report 94-4194, Denver, Colorado, (1995).

The USEPA requires that municipalities that have a population of 100,000 or greater obtain national pollutant discharge elimination system permits to characterize quality of their storm runoff. Final rules published by the USEPA (1990) require that municipalities prepare permit applications to include, among other information, the following: 1) characterization of the quality of storm runoff for three or more major storms at selected storm water discharge sites that represent different combinations of commercial, industrial, and residential land uses and 2) estimates of annual pollutant loads and event mean concentrations for selected constituents.
<u>Keywords:</u> storm water runoff, pollutants!

92. Gupta, S.K. and K.Y. Chen. "Partitioning of Trace Metals in selective Chemical Fractions of Nearshore Sediments." Environmental Letters, 10(2), 129-158 ,(1975).

A series of chemical extraction procedures are used to obtain data on the partitioning of trace metals among the various geochemical phases of sediments. These components include interstitial water, solubility of solid minerals, ions on exchange sites, metal carbonates, easily reducible phases, organics and sulfides, iron oxides and mineral residual fractions. In general, a mass balance of less than 10% deviation can be obtained. Experimental results show very small fractions of trace metals to be in the form of interstitial water or soluble ions. Trace metals in the exchangeable phase are almost negligible and those in the mineral residual phases range from 2.5% Cd for one sediment to 98% Cu for another. The non-residual trace metals content is found to increase with decreasing sand content.
<u>Keywords:</u> heavy metals, sediments, sequential extraction, bioavailability

93. Gippel, C.J. "Potential of turbidity monitoring for measuring the transport of suspended solids in streams." Hydrological Processes, vol. 9, pp. 83-97, (1995).

A literature review and lab experiments are presented on the factors that influence the relationship between turbidity measurements and suspended solids concentration. Two different types of instruments are considered: one (Hach 2100A) measures scattered light (nephlometric turbidity), and another (Partech 7000 3RP MKII) measures attenuated light (attenuance turbidity). As predicted by Mie theory, the turbidity measured by both instruments is maximal when the particle size is approximately equal to the wavelength of the light source (~1 micron). Water color (from organic material) increases the attenuance turbidity and decreases the nephlometric turbidity. The precise relationship between turbidity and SSC is likely to be site specific; however, the high frequency data obtainable by *in situ* turbidimeters can significantly improve sediment load measurements.
Keywords: SSC, Nephlometric turbidity, Attenuance turbidity, PSD
Stormwater Treatment Implications: This study demonstrates that using *in situ* turbidity instruments to estimate SSC in storm flows may not be practical. However, in situ turbidity devices may prove to be useful contaminant monitoring tools in their own right: (1) they are sensitive to the presence of organic material, and metals are often complexed with organic material in streams, (2) the wavelength of the light source can be, in principle, "tuned" to focus in on the particle sizes of most interest (e.g., a 300 nm would be sensitive to the presence of particles below 1 micron); (3) the ability of in situ devices to rapidly collect and log turbidity measurements could lead to a quantum leap improvement in our understanding of how particle and contaminant loadings change over the course of a storm at the influent and effluent of BMPs.

94. Gray, J.R., G.D. Glysson, L.M. Turcios and G. E. Schwarz. "Comparability of suspended-sediment concentration and total suspended solids data." US Geological Survey Water-Resources Investigations Report 00-4191, 14pp., (2000).

Two different methods for estimating the concentration of suspended solids—suspended-sediment concentration (SSC) and total suspended solids (TSS)—were compared using data from 3,235 paired samples collected from natural waters (e.g., creeks, rivers) in eight states during the 1980s and 90s. The TSS method underestimates the concentration of suspended solids, particularly when the sample contains particles greater than 0.062mm in diameter. SSC, on the other hand, is a more accurate and precise measure of suspended solids. The failure of TSS is attributed to biases that are introduced during the sub-sampling of the original sample.
Keywords: TSS, SSC, suspended solids, particle size distribution
Stormwater Treatment Implications: BMP performance may be underestimated when using TSS because this method will underestimate the concentration of larger particles--which are generally more efficiently removed by BMPs--in the influent and effluent. Furthermore, because of the accuracy and precision problems with TSS, regulatory limits for suspended solids in storm flows should be recast in terms of SSC.

95. Guy, H.P. "Laboratory theory and methods for sediment analysis: U.S. geological Survey Techniques of Water-Resources investigations." Book 5, chap. C1, (1969).

This report presents theories and methods used by the Water Resources Division for analysis of fluvial sediments to determine the concentration of suspended-sediment samples and the particle-size distribution of both suspended-sediment and bed material samples. Other analyses discussed include those for particle shape, mineral content, and specific gravity, the organic matter and dissolved solids of samples, and the specific weight of soils.

96. Granier, L., M. Chevreuil, A.M. Carru, and R. Letolle "Urban Runoff Pollution by Organochlorines (Polychlorinated Biphenyls and Lindane) and Heavy Metals (Lead, Zinc and Chromium)." Chemosphere, 121(9):1101-1107, (1990).

PCBs, lindane, Pb, Zn and Cr were analyzed at the outfall of a catchment served by a separate sewer system. Mean concentrations in the storm water runoff were respectively 130ng/l, 75ng/l, 140 μg/l, 730 μg/l, and 15 μg/l.
Keywords: urban runoff, heavy metals, pollutants, atmospheric deposition, pollutant sources.
Stormwater treatment implications: Reports the concentration of heavy metals and PAH compounds in urban runoff.

97. Greb, S.R., R.T. Bannerman. "Influence of particle size on wet pond effectiveness." Water Environmental Research, vol. 69(6), 1134-1138, (1997).

Water samples were collected during 16 separate storms from the influent and effluent of a 5670 m² wet detention pond designed to treat runoff from a predominantly residential urban area in Madison, Wisconsin. The pond effectively removed suspended solids (influent/effluent = 245/34.8 mg/L), total phosphorous (0.60/0.26 mg/L), but not total zinc (155/173 μg/L). Particles in the sand (.062-2.0 mm) and silt size ranges (0.004 to 0.062 mm) were more efficiently removed compared to particles in the clay size range (<0.004 mm). While the total amount of suspended solids decreased from influent to effluent, the fraction of particles in the clay size range more than doubled.
Keywords: urban runoff, detention, pond particle removal, settling, and particle removal.
Stormwater Treatment Implications: A wet pond will be more effective in shifting the PSD of storm water towards the smaller particle sizes, but it will be inefficient in the removal of the heavy metals and other pollutants usually associated with smaller particles.

98. Gromaire-Mertz, M. C., S. Garnaud, A. Gonzaleza, G. Chebbo. "Characterization of urban runoff pollution in Paris." Water Science and Technology, vol. 39(2), 1-8, (1999).

Water samples were collected from roofs, courtyards, and streets in central Paris, France. The dissolved (<0.45 μm) and particle (>0.45 μm) fractions were analyzed for SS, VSS, COD, BOD5, hydrocarbons, and metal concentrations (Cd, Cu, Pb,

Zn). Street runoff had the highest concentrations of SS (49-498 mg/L), oxygen consuming substances (48-964 mg/L), and hydrocarbons (115-4032 μg/L), while roof runoff had the highest heavy metal concentrations: Cd (0.1-32 μg/L), Cu (3-247 μg/L), Pb (16-2764 μg/L), Zn (802-38061 μg/L). It was found that except for hydrocarbons and lead, which were generally found in the particle fractions, the distribution of contaminants between dissolved and particulate fractions was variable. The settling velocities of particles in storm runoff were slow (30-50% of particle mass had settling velocities <0.002 cm/s).

Keywords: Heavy metals; hydrocarbons; organic matter; urban runoff; settling velocities, suspended solids.

Stormwater Treatment Implications: Settling alone is insufficient for runoff treatment, due to the relatively high level of dissolved pollution with relatively low settling velocities. Pretreatment with coagulant and/or filtration might be required. Erosion of Zn and Cu materials used in roof and gutter construction is a significant source of dissolved heavy metals in stormwater runoff. Groundwater infiltration of roof runoff could detrimentally impact groundwater quality.

99. Gromaire-Mertz, M.C., G. Chebbo, M. Saad. "Origins and characteristics of urban wet weather pollution in combined sewer systems: The experimental urban catchment Le Marais in Paris."Water Science Technology. Vol. 37, No. 1, 35-43,(1998).

The contributions of runoff, wastewater and sewer sediments to the water quality of combined sewer discharges were studied during dry weather and wet weather periods in Paris, France. During the dry weather periods suspended solids, COD, BOD_5, and VSS in sewer discharges were all correlated to daily flow. The study indicates that the quality of rainfall will worsen as it makes its way from rooftops, to yards, onto streets, to the combined sewer inlet, and then the outlet. The particulate bound pollution, as measured by COD and BOD_5 was found to be much worse (70-90%) for the outlet waters of the combined sewer than for runoff (20-90%). Pollutant in combined sewer discharges arise primarily from the erosion of in-sewer sediments and the adsorption of pollutants to particles.

Keywords: Combined sewer; field experiments; pollution; urban runoff; sewer sediments; wastewater, sediments, suspended sediments, particle size distribution.

Stormwater Treatment Implications: Storm water treatment strategies must include sewer network sedimentation as a major source of pollution in storm water discharges.

100. Gustafsson, O., P.M. Gschwend "Aquatic Colloids: Concepts, Definitions, and Current Challenges." Limnology and Oceanography, vol. 42, pp. 519-528, (1997).

Excellent review of the problems associated with establishing a definition of "colloids" that is relevant to the speciation, fate, and transport of chemical contaminants in aquatic systems. A tripartite classification of particles is proposed, including "dissolved", "colloidal", and "gravitoidal" . Colloids are defined as "any constituent that provides a molecular milieu into and onto which chemical can escape from the aqueous solution and whose environmental fate is predominantly

affected by coagulation-breakup mechanisms, as opposed to removal by settling."
Gravitoids are particles that are significantly affected by gravitational settling.
Dissolved substances provide no internal environment for a contaminant to partition
into, and their properties are essentially molecular in nature (e.g., ionized functional
groups can be treated as point charges, rather than in terms of surface potentials and
electric double layer theory). Operational approaches for separating particles based
on size (e.g., 0.5 micron cutoff between dissolved an particulate) is a poor approach
for distinguishing between dissolved/colloidal/gravitoidal categories. This is
because the nature of molecular material (e.g., globular vs linear proteins) can
determine whether the molecule has an internal environment (i.e., is dissolved or
colloidal), and the solids concentration can determine the critical particle size that
separates colloids and gravitoids. The idea that a critical particle size may depend
on solids concentration is based on the competition between different kinetic
phenomena; namely the transference of smaller particles up the particle size
spectrum by coagulation versus the gravitational sedimentation of larger particles.
While the rate of particle sedimentation does not depend on particle concentration
(rather the hydrodynamic drag on a particle and its weight), the former is a non-
linear (second-order) function of suspended solids concentration. Hence, operational
definitions of dissolved vs. particulate may not yield much information about
contaminant fate. This problem is obvious in the context of the so-called particle
concentration effect, in which the apparent distribution coefficient of a contaminant
between dissolved and particulate phases depends on the suspended solids
concentration; a result that is at odds with the thermodynamic basis of equilibrium
constants. Three different characteristics of colloids that might effect the solids
partitioning of colloids and their fate and transport are highlighted, including: (I) the
surface potential of the colloid can effect the equilibrium partitioning of ionic
contaminants (e.g., heavy metals), (ii) the organic content of a colloid can effect the
equilibrium partitioning of hydrophobic contaminants (e.g., PAHs), (iii) the
transference of colloids into gravitoids by coagulation can influence the impact of
settling on the transport of contaminants, and (iv) the internal environment of a
colloid can influence the type of chemical transformations (e.g., redox reactions,
photolysis, etc.) that a contaminant can undergo. Finally, it is noted that heavy
metals like copper may first associate with organic colloidal material, which then are
transferred to larger size classes by coagulation. Hence, the precise relationship
between heavy metals and gravitoids may involve colloidal intermediates.
Key Words: Heavy metals, particles, colloids, gravitiods.
Stormwater Treatment Implications: The proposed definition of particulate vs
dissolved would require rethinking current analytical approaches for measuring the
distribution of chemical contaminants in stormwater, and the appropriate treatment
approach. Several different separation methods are suggested, including separation
based on specific gravity (instead of particle size), using analytical
ultracentrifugation, and split-flow thin (SPLITT) cells.

101. **Hamilton, R.S., D.M. Revitt, R.S. Warren and M.J. Duggan "Metal Mass Balance Studies Within A Small Highway Dominated Catchment." The Science of the Total Environment, 59: 365-368, (1987)**

The levels of Pb, Cu, Cd and Zn in airborne suspended particulates, surface dust and storm water runoff, and their aerial deposition rates, are reported for a small highway dominated catchment.
Keywords: heavy metals, highway runoff, atmospheric deposition, pollutant sources
Stormwater treatment implications: Paper suggests that aerial deposition of particulates may be a significant source of heavy metals in stormwater flows.

102. **Harremoës, P. "Immediate and delayed oxygen depletion in rivers." Water Research, vol. 16, 1093-1098, (1982).**

Identifies three processes that contribution to oxygen depletion in rivers downstream of CSO discharges: mixing of overflow with river water, respiration of suspended organic matter in the water column, and respiration of organic matter deposited in the sediment. A mathematical model of these three processes is presented.
Keywords: Sedimentation, Oxygen Depletion, Storm Overflows.
Stormwater Treatment Implications: Stormwater discharges can cause oxygen depletion in receiving waters by several different mechanisms. Hence, removal of organic matter from stormflows is an important goal.

103. **Hewitt, C. N., and M.B.Rashed "Removal Rates of Selected Pollutants in the Runoff Waters from a Major Highway." Water Research, 26(3):311-319, (1992).**

The concentrations of cadmium, copper, lead, the organic compounds of lead and eight polycyclic aromatic hydrocarbons have been measured in surface drainage waters from a major rural highway in north-west England during a number of runoff events. The particulate phase ($>45\mu m$) contained $>90\%$ of the inorganic Pb, 70% of the Cu and ~56% of the Cd. The metal concentrations in suspended solids were similar to those in sediments.
Keywords: storm water runoff, highway runoff, heavy metals, PAHs
Stormwater Treatment Implications: Removal of suspended solids (e.g., by sedimentation) may significantly reduce the concentration of heavy metals in stormwater runoff.

104. **Howell, R. B. "Water pollution aspects of particles which collect on highway surfaces." California Department of Transportation Technical Report No. FHWA-CA-TL-78-22, (1978).**

This report was produced by Caltrans to gain a better understanding of the nature of constituents in pavement runoff waters at three sites during the winter of 1975 through the winter of 1977. The sample sites were located at I-405 Los Angeles, I-680 Walnut Creek, and Route 50 Placerville. Discrete samples were obtained at various times during storms and tested at the Transportation Laboratory in Sacramento. 34 different physical, chemical, and biological parameters were measured. Study found that during each storm there was a clear peak in the pollutograph where the pollutant concentration was greatest. A relationship appears

to exist between solid build up and antecedent dry weather period. COD, oil, and grease concentrations tended to vary with the magnitude of the runoff hydrograph although not proportionately.
Keywords: Water pollution, highway runoff, constituents in pavement runoff.
Stormwater Treatment Implications: Data presented in the report may be useful for developing optimal stormwater treatment strategies.

105.   Hvitved-Jacobsen, T. "The impact of combined sewer overflows on the dissolved oxygen concentration of a river." Water Research, vol. 16, 1099-1105,(1982).

This study was undertaken to determine the impact of combined sewer overflows on the dissolved oxygen concentration of a small river. Artificial sewer overflows, resembling existing overflows, were discharged through a ditch into the river Skravad in Jutland, Denmark. Two responses in stream oxygen concentrations during and after the passage of the discharge were observed over a 4 km stretch of the river. During the passage of the combined sewage, 4% of the total BOD was degraded immediately in the water phase and 35% was removed to the bottom of the river. A delayed effect on the water column DO level, caused by respiration of organic matter in the sediments, was observed. The transfer of organics into the sediments extends oxygen depletion over a longer period of time.
Keywords: Combined sewer overflow, dissolved oxygen
Stormwater Treatment Implications: Organic matter in combined sewer overflow can cause long-term oxygen depletion in receiving waters. Hence, removal of organic matter from stormflows should be considered in BMP design.

106.   Harrison, R.M., D.P.H. Laxen, and S.J. Wilson "Chemical associations of Lead, Cadmium, Copper and Zinc in Street Dusts and Roadside Soils." Environmental Science and Technology, 15: 1378-1383, (1978).

The chemical associations of Pb, Cd, Cu, and Zn in street dusts and roadside soils have been investigated by a sequential extraction procedure, which yields five fractions termed exchangeable, carbonate, Fe-Mn oxide, organic, and residual. In the soils and dusts examined, which covered a pH range of 6.9-8.4, only in the case of cadmium is there any appreciable proposition of total metal in the exchangeable fraction. Lead and zinc are predominantly associated with carbonates and Fe-Mn oxides, whereas copper is largely in organic association. The results are interpreted in terms of the environmental mobility and bioavailability of the metals.
Keywords: heavy metals, sequential extraction, bioavailability

107.   Hickey, M.G. and J.A. Kittrick "Chemical Partitioning of Cadmium, Nickel and Zinc in Soils and Sediments Containing High Levels of Heavy Metals." Journal of Environmental Quality 13(3): 372-376 ,(1984).

Three soils and a sediment which had undergone prior additions of heavy metals were sequentially extracted so that Cd, Cu, Ni and Zn could be partitioned into five operationally defined geochemical fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual. Metal recoveries were within ±10% of the independently measured total Cd, Cu, Ni, and Zn

concentrations. The highest amount of Cd was found in exchangeable fraction, but Cu was the only metal significantly associated with the organic fraction. Assuming that mobility and biological availability are related to the solubility of the geochemical form of the metals and decreases in the order of extraction, the apparent mobility and potential metal bioavailability for the highly contaminated soils and sediment is Cd>Zn>Cu=Ni

Keyword: sequential extraction, heavy metals, bioavailability.

108. **Hall, W.S., K.L. Dickson, F.Y. Saleh, J.H. Rodgers, Jr. "Effects of suspended solids on the bioavailability of chlordane to *Daphnia magna*." Archives of Environmental Contamination and Toxicology, vol. 15, 529-534, (1986).**

Experiments were conducted to assess the effect of suspended solids type and concentration upon the bioavailability of chlordane to *Daphnia magna*. Two types of solids were tested: montmorillonite clay (MC) containing 0% organic carbon and pond sediment containing 1.7% organic carbon. Experiments were conducted with a recirculating water system to keep particles in suspension during the 48 hr bioassay. Chlordane toxicity (and bioavailability) was reduced in the presence of >200-300 mg/L suspended solids, which reduced the aqueous concentration of chlordane. Suspended solids characteristics did not influence the results.

Keywords: Toxicity, suspended particles, water flea, bioavailability, nonpolar organics

Stormwater Treatment Implications: The bioavailability of organic toxicants is reduced by sorption onto suspended solids. Sorption efficiency is not strongly influenced by the organic carbon content of the particles, although particle size is likely to be an important factor.

109. **Hatch, A.C., G.A. Burton, Jr. "Sediment toxicity and stormwater runoff in a contaminated receiving system: consideration of different bioassays in the laboratory and field." Chemosphere, vol. 39, 1001-1017, (1999).**

Several field and laboratory tests were conducted to study the relationship between stormwater runoff effects and contamination at a site impacted by an urban storm sewer outfall. Water samples were collected during low and high flow conditions and tested in the laboratory for effects on survival, feeding rate, growth, and enzyme activity (IQ test). The responses of three freshwater species, *Daphnia magna* (water flea), *Hyallela azteca* (amphipod), and *Pimephales promelas* (fish) were compared. The laboratory results were also compared to the responses of the species exposed using *in situ* chambers that incorporated various exposure combinations (water only, at surface of sediment, sediment present in chamber). The influence of UV photoactivation and photodegradation was also assessed in the lab and field. Toxicity was detected in both types of exposures, but the *in situ* tests usually showed a greater frequency and magnitude of toxicity. In situ responses were also greatest in chambers that contained sediment and during high flow conditions. Fish survival and amphipod growth were the least sensitive test methods, no toxicity was detected in any of the exposures. Amphipod survival was the most sensitive and least variable test endpoint. Sublethal measurements of feeding rate and enzyme inhibition were more variable, these methods detected toxicity in a portion of the samples producing

effects on amphipod or water flea survival. The feeding results were confounded by excessive variability in the data and potential interferences with additional food supplied by sediment particles. Variation in UV light exposure had no effect on the biological responses, indicating that PAH-related phototoxicity was not significant in this system.

<u>Keywords:</u> toxicity, *in situ* testing, test methods, freshwater, stormwater, sediment, receiving water, water flea, amphipod, fish

<u>Stormwater Treatment Implications:</u> Stormwater effects are present under actual exposure conditions present in receiving water and sediment constituents contribute significantly to toxic effects. Invertebrate survival is a more reliable and sensitive measure of effects compared to fish survival of sublethal responses. Laboratory toxicity tests may underestimate the effects occurring in receiving water

110.   **Herricks, E., I. Milne. "A framework for assessing time-scale effects of wet weather discharges." Water Environment Research Federation, Alexandria, VA. 142 pp., (1998).**

This report summarizes the results of a multiyear study to develop guidance for the assessment of the biological effects of stormwater discharges. Stormwater discharges are episodic in nature and thus a different approach to biological assessment is recommended in comparison to whole effluent toxicity (WET) testing, where a continuous discharge is present. Three distinct time scales are of importance for stormwater discharges, and different assessment methods are needed to address them. These time scales are: 1) intra-event, which includes changes occurring within a storm event over times of seconds to hours; 2) event, which integrates changes occurring during a single event over time periods of hours to days; and 3) long-term, which integrates the effects occurring during the wet season and encompasses time periods of days to months. Additional issues that should be considered in designing an assessment program for stormwater include the location of the sampling sites within the watershed, variations in storm characteristics (e.g., return period, intensity), sampling design, which may vary depending upon the precision needed to satisfy data precision needs, and site specific characteristics of the receiving water area. There are no biological assessment methods that have been developed specifically for stormwater assessment, WET testing methods are usually applied. A variety of biological test systems, including biochemical responses, whole organisms tests, sublethal tests, and population/community responses, are reviewed relative to their suitability for application at one of the three time scales described above. Most test methods are unsuitable for evaluating intra-event impacts due to limitations related to response time, ecological relevance, precision, and cost. Two candidate methods, Microtox and the *Ceriodaphnia* IQ test were judged acceptable for intra-event assessment. The authors also describe and evaluate a modification of standard WET test methods to allow assessment of time scale responses. This method, called the Post-Exposure Lethal Exposure Time for 50% of the population (PE-LET50) assesses the latent effects of episodic exposures on organism survival and can be used to evaluate intra-event changes in toxicity. A framework for the application of time-scale toxicity testing is presented. The approach consists of several tiers, with the first tier consisting of basic screening tests at the time scales of interest. A second

tier of advanced testing is recommended if high/moderate toxicity is detected. Advanced testing includes dilution tests to estimate toxicity magnitude, and focused studies on sources, and causes of toxicity. The final tier of assessment includes confirmatory tests (*in situ* tests and biosurveys) to determine whether effects are occurring in the receiving water. Elements of the assessment framework were implemented in analyzing a series of storm events during 1994-96 at three locations in the United States. Key findings and recommendations from these studies include: 1) hydrograph data should be collected along with toxicity measurements, 2) a time scale approach that employs a battery of test species should be used, 3) toxicity measured in in-pipe samples are not always a good predictor of receiving water impacts, and 4) stormwater toxicity is strongly affected by site- and source-specific factors and probably not affected by regional-scale factors. Additional research in four areas is needed to support the development of a stormwater assessment framework: 1) the effects of variable exposure concentrations and frequency on organisms, 2) impacts of wet weather discharges on sediment contamination and dispersal, 3) the interaction of physical stress and habitat variables on time-scale toxicity, and 4) translation of new scientific understanding of the environment (physical, chemical, biological) into management tools.

Keywords: Stormwater, toxicity, time scales, receiving water, test methods

Stormwater Treatment Implications: Currently used methods for biological assessment are inadequate for determining intra-event changes in stormwater quality. Test methods that are responsive to exposure durations of minutes-hours are needed to measure changes in stormwater quality due to hydrological factors or treatment. A battery of test methods is needed to characterize stormwater impacts and metals have been identified as important toxic constituents.

111.   **ISO 643:1983** Steels -- Micrographic determination of the ferritic or austenitic grain size

112.   **ISO 728:1995** Coke (nominal top size greater than 20 mm) -- Size analysis by sieving

113.   **ISO 1953:1994** Hard coal -- Size analysis by sieving

114.   **ISO 2030:1990** Granulated cork -- Size analysis by mechanical sieving

115.   **ISO 2325:1986** Coke -- Size analysis (Nominal top size 20 mm or less)

116.   **ISO 2926:1974** Aluminium oxide primarily used for the production of aluminium -- Particle size analysis --Sieving method

117.   **ISO 2996:1974** Sodium tripolyphosphate and sodium pyrophosphate for industrial use -- Determination of particle size distribution by mechanical sieving

118.   **ISO 3118:1976** Sodium perborates for industrial use -- Determination of particle size distribution by mechanical sieving

119. **ISO 4150:1991** Green coffee -- Size analysis -- Manual sieving

120. **ISO 4497:1983** Metallic powders -- Determination of particle size by dry sieving

121. **ISO 4701:1999** Iron ores -- Determination of size distribution by sieving

122. **ISO 4783-1:1989** Industrial wire screens and woven wire cloth -- Guide to the choice of aperture size and wire diameter combinations -- Part 1: Generalities

123. **ISO 5915:1980** Sodium hexafluorosilicate for industrial use -- Determination of particle size distribution -- Sieving method

124. **ISO 6230:1989** Manganese ores -- Determination of size distribution by sieving

125. **ISO 6344-1:1998** Coated abrasives -- Grain size analysis -- Part 1: Grain size distribution test

126. **ISO6344-2:1998** Coated abrasives -- Grain size analysis -- Part 2: Determination of grain size distribution of macrogrits P12 to P220

127. **ISO 6344-3:1998** Coated abrasives -- Grain size analysis -- Part 3: Determination of grain size distribution of microgrits P240 to P2500

128. **ISO 7532:1985** Instant coffee -- Size analysis

129. **ISO 8130-1:1992** Coating powders -- Part 1: Determination of particle size distribution by sieving

130. **ISO 8220:1986** Aluminium oxide primarily used for the production of aluminium -- Determination of the fine particle size distribution (less than 60 mu/m) -- Method using electroformed sieves

131. **ISO 8486-1:1996** Bonded abrasives -- Determination and designation of grain size distribution -- Part 1: Macrogrits F4 to F220

132. **ISO 8486-2:1996** Bonded abrasives -- Determination and designation of grain size distribution -- Part 2: Microgrits F230 to F1200

133. **ISO 8511:1995** Rubber compounding ingredients -- Carbon black -- Determination of pellet size distribution

134. **ISO 8876:1989** Fluorspar -- Determination of particle size distribution by sieving

135. **ISO 9276-1:1998** Representation of results of particle size analysis -- Part 1: Graphical representation

136. **ISO 10076:1991** Metallic powders -- Determination of particle size distribution by gravitational sedimentation in a liquid and attenuation measurement

137. **ISO 11125-2:1993** Preparation of steel substrates before application of paints and related products – Test methods for metallic blast-cleaning abrasives -- Part 2: Determination of particle size distribution

138. **ISO 11127-2:1993** Preparation of steel substrates before application of paints and related products – Test methods for non-metallic blast-cleaning abrasives -- Part 2: Determination of particle size distribution

139. **ISO 11277:1998** Soil quality -- Determination of particle size distribution in mineral soil material – Method by sieving and sedimentation

140. **ISO 12984:2000** Carbonaceous materials used in the production of aluminium -- Calcined coke -- Determination of particle size distribution

141. **ISO 13319:2000** Determination of particle size distributions -- Electrical sensing zone method

142. **ISO 13320-1:1999** Particle size analysis -- Laser diffraction methods -- Part 1: General principles

143. **ISO 13321:1996** Particle size analysis -- Photon correlation spectroscopy

144. **ISO 13366-2:1997** Milk -- Enumeration of somatic cells -- Part 2: Electronic particle counter method

145. **ISO 14703:2000** Fine ceramics (advanced ceramics, advanced technical ceramics) -- Sample preparation for the determination of particle size distribution of ceramic powders.

146. **Jewell, T. K., D. D. Adrian and F. A. Digiano. "Urban stormwater pollutant loadings." Publ. No. 114, Water Resources Research Center, University of Massachusetts, Amherst,(1980).**
Presents an analysis of water quality data from 261 storm events, 26 basins, in 12 geographical areas. Report suggests that it is not possible to derive general pollutant washoff functions for most areas. A methodology is developed to predict stormwater pollutant washoff functions for individual watersheds based on local water quality data.
Keywords: Stormwater, washoff, pollutant loadings, predictive techniques
Stormwater Treatment Implications: Stormwater quality models must be tailored to individual field sites based on water quality data collected over a number of storm events.

147.   Jiang, Y., Kummerow, A., Hansen, M. "Preparative Particle Separation by Continuous SPLITT Fractionation."Journal of Microcolumn Separations, 9(4), 261-273, (1997).

Continuous operation of split-flow thin-cell fractionation (SPLITT) is examined using silica and artificial diamond particles. Flow rates between 2 μL and 93 μL and concentrations ranging from 0.1% (w/v) to 5% (w/v) for silica and 0.1% (w/v) to 1% (w/v) for diamonds. For silica, concentrations 0.1% (w/v) to 2% (w/v), and for diamonds, concentrations 0.1% (w/v) to 0.2% (w/v), yielded good results determined from size analysis of scanning electrons micrographs.
Keywords: split-flow thin-cell fractionation, preparative scale particle separation
Stormwater Treatment Implications: Laboratory technique for size fractionation of slurry samples. Not suitable for field deployment.

148.   Jones, H.K., Giddings, J.C. "Separation and Characterization of Colloidal Materials of Variable Particle Size and Composition by Coupled Column Sedimentation Field-Flow Fractionation."Analytical Chemistry, 61, 741-745, (1989).

Coupled column sedimentation field-flow fractionation (SdFFF), in which a narrow fraction from one run is reinjected for a second SdFFF run under different conditions is tested. Different carrier fluid densities (sucrose) were used in successive SdFFF stages to fractionate a binary mixture composed of polystyrene (PS) and polyvinylchlorids (PVC) latex particles. The main problem was transferring enough of a sample fraction from the first stage to the second to provide adequate detector signal. Three different ways to address inadequate population size were: split-outlet concentration, on-channel concentration, and intermediate centrifugation. Results were reasonable but methodology requires added laboratory.
Keywords: coupled field-flow fractionation, low concentration, weak detector signal.
Stormwater Treatment Implications: Demonstrates coupled application of field-flow-fractionation for synthetic colloids. Limited use for laboratory analysis. Not suitable for field deployment.

149.   Jones, H.K., Phelan, K., Myers, M.N., Giddings, J.C. "Colloid Characterization by Sedimentation Field-Flow Fractionation." Journal of Colloid and Interface Science, 120(1), 140-152, (1987).

Split-flow sedimentation field-flow fractionation is evaluated using a complex colloidal population whose particles vary in both diameters and density. By this methodology the outlet stream of the FFF channel is split along a specified flow plane to yield two distinguishable flow laminae whose contents enter two different outlet substreams. By adjusting carrier fluid density using sucrose the colloids driven by centrifugation will divide into two classes, depending on competing inertial and buoyancy forces. These two classes then undergo FFF migration and separation followed by elution into two different substreams. The method has been verified for polystyrene particles.
Keywords: sedimentation field-flow fractionation, split flow, complex distributions.

Demonstrates application of split-flow sedimentation field-flow-fractionation for synthetic colloids. Carrier fluid density is modified. Useful for laboratory analysis. Not suitable for field deployment.

150. Karouna-Renier, N.K., D.W. Sparling. "Relationships between ambient geochemistry, watershed land-use and trace metal concentrations in aquatic invertebrates living in stormwater treatment ponds." Environmental Pollution, vol. 112, 183-192, (2001).

Stormwater treatment ponds provide habitat for wildlife in many areas, raising concern about the impacts of contaminated pond sediments. Previous studies by others have measured elevated concentrations of metals in fish and tadpoles living in ponds near roadways and the concentrations appeared to be proportional to highway use. Water, sediment, and invertebrates from 20 treatment ponds in Maryland were collected for chemical analysis. The ponds reflected three types of urban land use: commercial, highway, and residential. Two of the study sites were natural ponds that had essentially no urban development in the watershed. The sediments in all ponds were predominantly (75%) sand. No significant differences in aqueous (dissolved) or sediment metals concentrations were present among land uses. Dissolved Cu and Zn in the urban ponds tended to be greater than the natural ponds, however, and sediment Pb and Zn concentrations in commercial ponds were higher than in the other land uses. Tissue Cu and Zn concentrations in odonates from commercial ponds were significantly higher than concentrations in the other land uses. Tissue concentrations in invertebrates from highway ponds tended to be greater than those from natural ponds, but the differences were not statistically significant. Tissue lead concentrations were positively correlated with water turbidity, suggesting that particle ingestion was an important route of exposure to this metal. Tissue Cu and Zn concentrations were positively correlated with the dissolved concentrations of these metals and inversely correlated with dissolved magnesium. Though elevated in invertebrates, the tissue metal concentrations were below threshold dietary exposure values for toxicity to fish.
Keywords: Stormwater pond, sediment, receiving water, bioaccumulation, invertebrate, metals, highway runoff
Stormwater Treatment Implications: Metals associated with highway runoff particles are bioavailable to benthic organisms. Most of the sediment in stormwater treatment ponds is sand, suggesting that these systems are ineffective in trapping the small particles that may carry the highest concentrations of contaminants. Sediment contamination and bioaccumulation within treatment ponds is very complex and influenced by numerous geochemical factors, and thus difficult to predict. Periodic monitoring of individual ponds is needed to assess their effectiveness and determine the risk to wildlife.

151. Karouna-Renier, N.K., D.W. Sparling. "Toxicity of stormwater treatment pond sediments to *Hyallela azteca* (Amphipoda)." Bulletin of Environmental Contamination and Toxicology, vol. 58, 550-557, (1997).

Sediments from nine stormwater treatment ponds in Maryland were collected and analyzed for toxicity, TOC, AVS, and simultaneously extracted metals (Cu, Cd, and Ni). Treatment ponds were selected to represent inputs from either highway, residential, or commercial land uses and all had been in use for 3-5 years. A

reference pond that received no urban discharges was also sampled. Toxicity was measured using 10-day amphipod (*Hyallela azteca*) exposures to the sediment using an intermittent water renewal system; the toxicity endpoints were survival, mean individual dry weight, and mean individual length. No adverse effects to amphipods were detected in any of the samples. Some pond sediments produced significantly enhanced amphipod growth, possibly due to the organic content of the sediments providing an additional food source to the test animals. TOC concentrations were not elevated in the sediment samples and concentrations of Cd and Ni were below detection limits of 0.2 μg/g and 5 μg/g, respectively. Cu concentrations ranged from <1 μg/g to 7.2 μg/g while AVS ranged from <2 μg/g to 76 μg/g. Ratios of Cu to AVS were <1 for all samples, indicating that sediment-associated metals were not likely to be bioavailable. AVS was positively correlated with amphipod survival and length, which may reflect the beneficial role of AVS in limiting metal bioavailability. This study was conducted in dry weather on relatively young ponds, so the results may not be applicable to wet weather deposition or older systems.
Keywords: Toxicity, freshwater, amphipod, stormwater pond, sediment, AVS, metals, highway runoff.
Stormwater Treatment Implications: Treatment ponds utilizing natural processes may be effective at reducing the toxicity of stormwater particles. The study was not well-designed to address treatment effectiveness, however; wet weather events were not targeted and no measurements of sediment quality before deposition in the pond were made.

152. **Kersten, M., and U. Forstner "Chemical Fractionation of Heavy Metals in Anoxic Estuarine and Coastal Sediments." Water Science and Technology, 18: 121-130, (1986).**

Chemical extraction experiments for estimating characteristic particulate binding forms of heavy metals in anoxic marine and freshwater sediments were carried out under both the presence and absence of atmospheric oxygen during the analytical procedure. Storage methods including aeration of anoxic sediments do not preserve the initial fractionation patterns of heavy metals and may both increase (Ni, Pb, Cu, Zn, Cd) and decrease (Fe, Mn) their mobility. Elutriate tests of methanogenic freshwater sediments from Hamburg harbor basins show that metals with increased carbonatic fractions (Fe, Mn) and those with predominantly sulphidic/organic fractions (Zn, Cu< Cd) are particularly sensitive to sample aeration.
Keywords: heavy metals, sequential extraction, sediments, particulates, bioavailability.

153. **Knott, J.M., C.J. Sholar and W.J. Matthes. "Quality assurance guidelines for the analysis of sediment concentration by U.S. Geological Survey Sediment Laboratories: U.S. Geological Survey Open-File Report." 93-33, 30 p., (1992).**

Report describes procedures for preserving suspended-sediment sample integrity, calibrating and maintaining laboratory equipment, analyzing samples, internal QA/QC, and providing data security.
Keywords: Suspended-sediment, concentration, quality control, quality assurance

154.   Knott, J.M., G.D. Glysson, B.A. Malo and L.J. Schroder."Quality assurance plan for the collection and processing of sediment data by the U.S. Geological Survey, Water Resources Division: U.S. Geological Survey Open-File Report" 92-499, 18 p., (1993).

Report describes quality assurance and quality control practices for collecting sediment data.
Keywords: sediment data, quality assurance, quality control, transport, erosion.

155.   Krein, A. and Schorer, M. "Road Runoff Pollution by Polycyclic Aromatic Hydrocarbons and its Contribution to River Sediments." Water Research, 34, 16, 4110-4115, (2000).

Freshwater surface sediments, street dust, and street runoff were sampled at the Olewiger Bach (Germany) catchment. Samples were collected in solvent-washed 2L glass bottles with glass tops. Fine sand fraction was wet-sieved (63-200 μm). Centrifugation was used to concentrate the fraction smaller than 63 μm. Size fractionation using an elutriation process yielded the following size fractions: < 2 μm, 2-6.3 μm, 6.3-12.5 μm, 12.5-20 μm, and 20-63 μm. Elutriation involves suspending the sample in an upward flow such that particles with settling velocities larger than the upward velocity will settle while all other particles are carried over to the next separation reactor having a lower upward velocity. By matching the upward velocities with particle settling velocities from Stoke's law, the size fraction retained can be calculated for each stage. Particle size was confirmed using particle size measurements. All samples were dispersed in $Na_4P_2O_7$ and agitated for one hour. Particle fractionation took 30 hours per sample.
Keywords: Environmental samples, fractionation, sequential-stage elutriation.
Stormwater Treatment Implications: Technique for size fractionation of particulate samples.

156.   Kaighn, R.J., and S.S. YU. "Testing of Roadside Vegetation for Highway Runoff Pollutant Removal." Transportation Research Record, N1523, 116-123, ISSN: 0361-1981, (1996).

Evaluates the ability of grassy swales to remove pollutants from highway runoff. Pollutant removal in a short buffer strip is examined. Pollutants monitored included total suspended solids, chemical oxygen demand, total phosphorus and total zinc.
Keywords: highway runoff, pollutants, particulates, BMPs, swales
Stormwater Treatment Implications: A well-designed buffer strip and swale-check dam system can lead to pollutant removal and is preferable to a curb and gutter system.

157.   Kerri, K.D., J.A. Racin, and R.B. Howell. "Forecasting Pollutant Loads From Highway Runoff." Transportation Research Record: 39-46 ,(1985)

Regression equations for forecasting pollutant loads in runoff from highways are developed. This approach is tested using water quality data collected during storm seasons at paved urban highway sites in California. Constituents analyzed include total lead, total cadmium, and total zinc. The number of vehicles during the storm was evaluated and accepted as a satisfactory independent variable for estimating the

loads of total lead, total zinc. Application of this approach is limited to highways with average daily traffic of at least 30,000 vehicles.
Keywords: pollutants, highway runoff, heavy metals
Stormwater Treatment Implications:!It may be possible to predict the loading of some contaminants in highway runoff using regression on local water quality data.

158.   **Krein, A. and M. Schorer. "Road Runoff Pollution by Polycyclic Aromatic Hydrocarbons and its Contribution to River Sediments." Water Research 34(16): 4110-4115, (2000).**

The impact of particle bound pollutants from road runoff on river water and sediment quality was studied. Rainfall intensity is responsible for the wash load, whereas the grain size distribution is controlled by the amount of rainfall and sorting processes that occur near street traps. The concentrations of suspended heavy metals show a familiar inverse relationship to particle size in both road runoff and river bottom sediments; however, the relationship between pollutant levels and particle is less clear in the case of polycyclic aromatic hydrocarbons (PHAs) .
Keywords: storm water runoff, urban runoff, PAHs, heavy metals, particle size distribution, pollutant load
Stormwater Treatment Implications: Treatment design should consider the fact that different pollutants (e.g., heavy metals vs. PAHs) can exhibit different relationships to particle size.

159.   **Lopes, T.J. and S.G. Dionne. "A Review of Semivolatile and Volatile Organic Compounds in Highway Runoff and Urban Stormwater." US. Geological Survey Open-File Report, OFR98-409, 67p. ,(1998).**

The objectives of this review were to evaluate the quality of existing data on SVOCs and VOCs and to summarize significant findings. This was not an exhaustive review of all studies that contain information on SVOCs and VOCs, but rather a review of studies that focused primarily on SVOCs and VOCs in highway runoff, urban storm, and sedimentation.
Keywords: highway runoff, urban runoff, PAHs, organics, sources

160.   **Lee,H., Kim Ratanathanawongs Williams,S., Giddings, J. C. "Particle Size Analysis of Dilute Environmental Colloids by Flow Field-Flow Fractionation Using an Opposed Flow Sample Concentration Technique.", Analytical Chemistry, 70(13), 2495 -2503, (1998).**

An on-line concentration method has been developed for the analysis of dilute suspensions of macromolecules and particles by flow field-flow fractionation (FFF). This method, termed opposed flow sample concentration (OFSC), uses two opposing flowstreams to focus sample into a narrow band near the inlet of the flow FFF channel. Large sample volumes (up to 1 L) have been successfully loaded, concentrated, and separated in a 1 mL volume flow FFF channel. Concentration factors as high as 10^5 have been achieved. The effectiveness of OFSC flow FFF was demonstrated by a separation of river water colloids.
Keywords: Opposed flow field-flow fractionation, large samples.

Stormwater Treatment Implications: Demonstrate fractionation of river water colloids. Potentially very useful for laboratory analysis. Not suitable for field deployment.

161. **Logan, B.E. "Comment on Investigation of a Sequential Filtration Technique for Particle Fractionation." Environmental Science and Technology, 29, 8 2166-2177, (1995).**

Discusses reasons for difficulties in obtaining accurate size fractions from sampled bottom sediments in paper by Droppo et. Al. (Droppo, I.G., Krishnappan, B.G., Rao, S.S. and Ongley, E.D.: Investigation of a Sequential Filtration Technique for Particle Fractionation", Environmental Science and Technology, 29, 2, 546-550, (1995).)
The reasons given include particle-particle and particle-filter interactions predicted by filtration theory. Stickiness or aggregation efficiency is the main reason for size fraction broadening.
Keywords: Environmental samples, fractionation, sequential-stage filtration, model.
Stormwater Treatment Implications: Technique for size fractionation of particulate samples. Not suitable for field deployment. Not recommended for laboratory use.

162. **Lara-Cazenave, M.B., V. Levy, A. Castetbon, M.Potin-Gautier, M. Astruc, E. Albert. "Pollution of urban runoff waters by heavy metals. Part I: Total Metal" Environ. Technol. Vol. 15, pp. 1135-1147, (1994).**

Article is in French, and so the English abstract is reproduced here: "The metallic content (Cd, Cu, Pb, Zn) of urban runoff waters has been studied after phase separation by 0.45 micron filtration, as well as global parameters. Sequential sampling has been performed during seven important rainfalls in a single residential area in 1991 and 1992. A minor first flush effect has been noted. The better part of the metallic pollutants was in the particulates at quite high concentrations (Cd 5 µg/g; Cu 400 µg/g; Pb 700 µg/g; and Zn 2000 µg/g). A study of the multiparameter correlation's evidenced strong links between COD, BOD5, Suspended Solids, and Cu and Pb concentrations in the particulate phase. Conductivity was not correlated to any parameter."
Keywords: Heavy metals, stormwater runoff, first flush.
Stormwater Treatment Implications: According to abstract, particulate-associated metals are present at high concentrations, implying that treatment should focus on particle removal.

163. **Laxen, D.P.H. and R.M. Harrison "The Highway as Source of Water Pollution: An Appraisal with Heavy Metal Lead." Water Research, 11: 1-11, (1977)**

Factors influencing the impact of lead in highway runoff on receiving water quality are discussed, and available information on sources are reviewed. The concentration of lead in highway runoff can reach levels far in excess of those normally encountered in surface waters. The present inadequate understanding of the physiochemical forms of lead in polluted and natural waters is highlighted.
Keywords: highway runoff, sources, heavy metals

<u>Stormwater Treatment Implications:</u> An adequate understanding of the physiochemical forms of lead needs to be obtained so that treatment systems targeting led contamination can be developed.

164. Legret, M. and C. Pagotto "Evaluation of Pollutant loadings in the runoff Waters from a Major Rural Highway." The Science of the Total Environment 235: 143-150 ,(1999).

The quality of pavement runoff water from a 275m long section of a highway motorway is studied for 1 year, during which approximately 50 rain events occurred. Two pollution patterns are identified. Chronic pollution in the runoff is characterized by the presence of suspended solids, chemical oxygen demand, total hydrocarbons, zinc and lead. The second winter pattern, which derives from the use of deicing salts, includes chlorides, sulfates, suspended solids and heavy metals.
<u>Keywords:</u> heavy metals, highway runoff, pollutant loads
<u>Stormwater Treatment Implications:</u> Any stormwater treatment plan must account for both chronic and seasonal pollution, and the fact that different pollutants are associated with each.

165. Lion, L.W. R.S. Altmann, and J.O. Leckie "Trace Metal Adsorption Characteristics of Estuarine Particulate Matter: Evaluation of Contributions of Fe/Mn Oxide and Organic Surface Coatings." Environmental Science and Technology, 16(10): 660-8666 ,(1982).

Metal solubilization resulting from specific chemical extractions has frequently been employed to define the solid-phase association of trace metals in naturally occurring particulates. Adsorption of Cd and Pb onto the residual surface phase after extraction yields supporting evidence with respect to the influences of extracted components on metal-binding properties. Trace metal binding to surficial sediments in the South San Francisco Bay estuary was examined with the aid of chemical extractants and adsorption techniques. System composition-dependent adsorption of Cd and Pb onto estuarine sediments behaved in a manner analogous to adsorption onto single-phase hydrous oxide surfaces. Extraction results show Cd, Cu and Pb associate with operationally defined organic and/or metal (Fe, Mn) oxide surface coatings. Changes in the Cd and Pb adsorption behavior after specific extractions were consistent with the hypothesis that Fe/Mn hydrous oxides and organic coatings substantially control the sorptive behavior of estuarine particulate matter.
<u>Keywords:</u> heavy metals, sediments, particulates, sequential extraction
<u>Stormwater Treatment Implications:</u> Fe/Mn hydrous oxide and organic coatings could be used to control the behavior of particulate matter in stormwater runoff.

166. Lucas-Aiguier, E., GT. Chebbo, J. Betrand-Krajewski, B. Gagne, P. Hedges. "Analysis of the methods for determining the settling characteristics of sewage and stormwater solids." Water Science and Technology, vol. 37, 53-60, (1998).

Study compares velocity grading curves generated for the same wastewater/stormwater samples using four different standard methods: UFT, Cergrene, Aston, Camp. The different protocols yielded very different velocity grading curves on the same samples. The UFT method gave the largest velocities,

presumably due to the fact that this method only takes into account the fall velocity of settleable solids. The underlying reasons for all the variability observed is not well explored.

Keywords: Velocity grading curves, Stokes law, settling basins

Stormwater Treatment Implications: The use of standard methods to generate velocity grading curves for settling basin design could be unreliable. A precise, accurate, and internationally accepted method for developing these curves is needed.

167.   Lygren, E., E. Gjessing, L. Berlind. "Pollution transport from a highway." The Science if the Total Environment, 33, 147-11259, (1984).

Reports on metals and PAH levels in dustfall and snow/rain runoff from a highway in Norway with an average traffic density of 8000 vehicles per day. Studded tires erode asphalt and are responsible for a significant fraction of the dust fall out around roads (20-50 g/km/vehicle). The dust is enriched in PAH; equal amounts of some metals (e.g., Pb) are transported by dust fall and snow/rain runoff. The majority of the dustfall-associated metals deposit within 7m of the highway. PAH and metals appear to accumulate in snow, and then are released to receiving waters during the spring.

Keywords: Pavement dust, micropollutants, snowmelt, highway runoff

Stormwater Treatment Implications: Dustfall could be a significant source of pollutant loading in storm and snow runoff, particularly in areas where studded tires are common. BMPs that reduce dustfall could lead to water quality improvement.

168.   Lygren, E., E. Gjessing, and L. Berglind "Pollution Transport from a Highway." The Science of the Total Environment, 33: 147-159,(1984).

A three-year program, sponsored by the Norwegian road directorate, was aimed at characterizing the nature and the fate of particulate matter from a highway. Particulate matter was characterized with respect to particle size distribution, heavy metal concentration and contents of organic micro pollutants, such as PAHs. The majority of pollutants are deposited within 5-25 m from highway sources. A significant amount of the pollutant load is released from snowmelt in the spring

Keywords: highway runoff, pollutants, particulate, atmospheric deposition

Stormwater Treatment Implications: Storm water treatment strategies may need to include runoff not only from the road surface but from the surface of the roadsides up to 25 m from the road.

168.   Maestri, B., M.E. Dorman, and J. Hartigan "Guide for Mitigation of Highway Stormwater Runoff Pollution." The Science of the Total Environment, 59:467-476, (Jan 1987).

A synopsis of interim guidelines for the design of BMPs for the removal of pollutants from highway storm water runoff. Three general types of management measures are identified as effective in treating highway runoff: vegetative controls, detention basins, and retention measures.

Keywords: highway runoff, storm water runoff, BMPs.

Stormwater Treatment Implications: Pollution from highway runoff can be controlled by vegetative control, wet detention basins, infiltration systems, and wetlands.

169.   **Makepease, D. K., D. W. Smith, and S. J. Stanley. "Urban Stormwater Quality: Summary of Contaminant Data."Critical Reviews in Environmental Science and Technology, 25(2):93-139,(1995).**

A literature review on available contaminant data for storm water. The reported concentrations are placed in the context of pertinent guidelines, regulations, and levels that have been reported to cause possible adverse receiving water quality impacts.
Keywords: storm water quality, storm water, pollutants, microorganisms
Stormwater Treatment Implications: Paper summarizes pollutant types and concentrations typically found in stormwater runoff.

170.   **Maltby, L., D.M. Forrow, A.B.A. Boxall, P. Calow, C.I. Betton. "The effects of motorway runoff on freshwater ecosystems: 1. Field study." Environmental Toxicology and Chemistry, vol. 14, 1079-1092, (1995a).**

Seven streams receiving drainage from the M1 roadway in Northern England were surveyed for a period of 12 months. Dominant PAHs were phenanthrene, pyrene, and flouranthene; dominant metals were zinc, chromium, and lead. Results indicated that quality of both receiving waters and sediments were altered at stations <100m from point-source input of roadway runoff. Elevated levels of chloride and sulfate were also found, together with a decrease in the diversity of macroinvertebrate assemblages at the stations receiving motorway runoff.
Keywords: Road runoff, Sediment contamination, Benthic communities, Hydrocarbons
Stormwater Treatment Implications: Pollutants released from highway runoff causes shifts in macroinvertebrate diversity in receiving waters.

171.   **Maltby,L., A.B.A. Boxall, D.M. Forrow, P. Calow, C.I. Betton. "The effects of motorway runoff on freshwater ecosystems: 2. Identifying major toxicants." Environmental Toxicology and Chemistry, vol. 14, 1093-1101, (1995b).**

Origin of highway toxicity was investigated using a benthic amphipod *Gammarus pulex*. Sediments contaminated with motorway runoff were slightly toxic; however, contaminated stream water did not appear to be toxic to the amphipod. Most of the sediment toxicity was attributed to the presence of hydrocarbons, specifically PAHs; heavy metals did not appear to play a significant role in the toxicity of the sediment and water.
Keywords: Motorway runoff, Sediment toxicity, Hydrocarbons, TIE
Stormwater Treatment Implications: PAHs in highway runoff should be targeted for removal by treatment systems, since these contaminants contribute to downstream sediment toxicity.

172.   Marsalek, J., B. Brownlee, T. Mayer, S. Lawal, and G.A. Larkin "Heavy Metals and PAHs in Stormwater Runoff from the Skyway Bridge, Burlington, Ontario." Water Quality Research Journal, 32(4): 815-827,(1997).

Samples of storm water runoff from the skyway bridge in Burlington, Ontario, were analyzed for 5 heavy metals (Zn, Pb, Ni, Cu, and Cd) and 14 polycyclic aromatic hydrocarbons (PAHs) in dissolved and particulate-bound phases. Of the metals, the highest event mean concentrations in whole-water samples were those for Zn, Cu, and Pb. PAH event-mean concentrations in whole water samples ranged from 0.015-0.5 µg/l for individual compounds. Dissolved phase PAHs represented less than 11% of whole water concentrations.
Keywords: highway runoff, heavy metals, PAHs, dissolved fraction, particulate fraction, pollutant loads
Stormwater Treatment Implications: Treatment schemes should focus on the removal of heavy metals from stormwater runoff.

173.   Meister, J.F., S. Kefer. "Stormwater quality from an urbanizing watershed." In *Urban Stormwater Quality, Management and Planning* (Edited by Yen, B. C.), Water Resources Publication, Colorado, U.S.A., (1982).

Runoff samples from 12 storms (April through December 1979) were analyzed for physical, chemical and biological characteristics at a 385 acre watershed in Southern Illinois. Land-use in the watershed consists of urban (50%) and segregated non-urban (50%). Urban runoff had considerably higher concentrations of contaminants then non-urban pollution. All contaminants demonstrated a first flush except for fecal coliform bacteria, which steadily increased over a given storm event.
Keywords: Urban runoff, non-urban runoff, anthropogenic activity, urban storm sewers.
Stormwater Treatment Implications: Land-use affects the nature of pollutants released during storms.

174.   Moe, R.D., J.A. Bullin, and M.J. Lougheed "Atmospheric Particulate Analysis and Impact of Highway Runoff." Texas State Dept. of Highways and Public Transportation, (1982).

This experiment was designed to monitor water quality, air quality, traffic and meteorology along an elevated, impervious section of interstate highway in Dallas, Texas, with a closed storm sewer system. Volume of flow, rainfall, and pollutants discharged were monitored automatically during rainstorms. Particulates were sampled at three locations.
Keywords: water quality, atmospheric deposition, highway runoff, particulates, pollutant load
Stormwater Treatment Implications: Management measures to improve the quality of highway runoff should consider air quality, storm intensity, seasonal meteorology, and urban surface construction material.

175. Moore, R.A., and B. T. Butler. "Impacts of Highway Runoff on Surface Water Drinking Supplies." Proceedings of the 22nd Annual Conference on Integrated Water Resources Planning for the 21st Century. Cambridge, MA, USA. ASCE: 380-383,(1995).

This paper provides an overview of three issues that are frequently the subject of discussion between transportation officials and environmental regulators: the impacts of deicing chemicals, conventional pollutants, and spills on public surface water drinking supplies.
Keywords: highway runoff, pollutants
Stormwater Treatment Implications: The potential impact of highway pollutants on surface drinking water supplies should be considered in the development of appropriate stormwater management strategies.

176. Morrison, G.M., D.M. Revitt, J.B. Ellis, G. Svensson, P. Balmer "Transport mechanisms and processes for metal species in a gullypot system." Water Research, vol. 22, pp. 1417-1427, (1988).

Good review of the role that water chemistry can play in mobilizing metal contaminants in stormwater runoff. Atmospheric fallout and stormwater runoff from a college (Chalmers University of Technology, Goteborg) parking lot in Sweden was sampled and analyzed for heavy metals (Cd, Cu, Pb, Zn) during 6 storms between July and September of 1984. Several possible sources and transport pathways are evaluated, including: 1) atmospheric fallout, 2) acid rain mobilization of road dusts, 3) role of road dust in pH buffering, 4) pH/Surface area dependent suspended solid metal transport, 5) metal sequestering in gullypot liquor between storms, and 6) contribution of gully pot liquor and sediments to metals in the gullypot outflow. A scheme for measuring "dissolved" and "particulate" metals is presented, and an effort is made to determine how strongly the metals are complexed and solubilized in the dissolved and particulate phases, respectively. Atmospheric fallout is found to be a significant source of dissolved (Pb and Cu) and particulate (Cu and Cd) metals. The road surface may limit the transfer of atmospheric fallout into runoff by adsorption and complexation of metals with coarser solids and by changing the chemical speciation of metals upon road contact. Acid rain can facilitate the transfer of metals into the soluble phase by dissolution and surface protonation, as appears to be the case for Cd. Indeed, road dust particles smaller than 1000 microns were shown to contain a high proportion of exchangeable Cd (up to 100%), Cu, and Zn all of which may be solubilized by acidic rainfall. Lead, on the other hand, appears to be more strongly sediment associated (i.e., not as easily solubilized by acid rain). Authors point out that pH buffering in gullypots affects metal speciation. The amount of particle-associated metals in runoff can be affected both by the higher specific surface area associated with smaller particles, and a hydrodynamic sorting effect described by Harrison and Wilson (1983). It is hypothesized that hydrodynamic sorting and surface area effects are important at high and low suspended solids concentrations, respectively. Authors present evidence that Pb exhibits a surface area dependent metal uptake mechanism at the field site. One possible mechanism for metal transport through a drainage system envisions the following: 1) initial solubilization of metals during acid rain fall, and 2) subsequent pH buffering by road

salts causes hydrodynamically sorted fines to uptake free metals thus leading to a metal enrichment of the fine particles. Besides pH, other important water quality parameters include exposed organic carbon and hydrous Fe and Mn oxide particulate surfaces that can uptake metals, and a change in redox potential or an increase in ionic strength which can reduce metal uptake on solid surfaces. The concentration of all four metals in the gully pot liquor increased with time since the last storm. Using a Michaelis/Menten type formulation, authors estimate the characteristic time for each metal to reach half its saturation value, which range from 1 to 122 hours. The maximum metal concentrations for two dry periods were 406.5 and 79.4 µg/L (Zn), 13 and 4 (Cd), 192.3 and 120.5 (Pb), and 454.5 and 277.8 (Cu). Authors suggest that the fast release of Zn and Cu may be due to acid dissolution, while the slower release of Cd and Pb may be due to bacterial activity; e.g., complexation of metals by bacterial extra-cellular polymers, as has been demonstrated for *Pseudomonas* sp. in Ellis (1985) and Rudd et al. (1984). As a result of metal accumulation in the gullypots, they represent a significant source of heavy metals during storms. Most of the metals are released in the initial phases of the storm as gullypot liquor and interstitial waters are entrained in the flow.

Keywords: Heavy metals, stormwater treatment, water chemistry

Stormwater Treatment Implications: The sequestering, speciation, and fate of metals captured in roadside sedimentation basins, such as gullypots, are dictated by water chemistry (pH, ionic strength, redox intensity, organic carbon), physical processes (hydrodynamic sorting, specific surface area available, mass transfer limitations), and biological processes (complexation of metals by bacterially generated extracellular polysaccharides). Study demonstrates that sediment and liquor accumulation in basins between storms can serve as a significant source of metals in storm water runoff, particularly for large rain events. Furthermore, the soluble fraction of metals in the gullypot outflow are in the bioavailable chelex removable form, implying that this source of metals could detrimentally impact receiving water ecology. Ideally, gullypots and similar detention basins should be cleaned at 4-7 day intervals to prevent build-up of metals.

177. Mulliss, R., D.M. Revitt and R.B.E. Shutes. "The impacts of discharge from two combined sewer overflows on the water quality of and urban watercourse." Water Science and Technology, vol. 36(8-9), 195-199, (1997).

This paper compared the water quality impacts of discharges from two combined sewer overflows and two surface water outfalls in a 4 km stretch of Pymmes Brook in North London during dry weather conditions and wet weather conditions. The authors found that during storm events, average concentrations of BOD, total ammonia, suspended solids, chloride, zinc, copper, lead and cadmium were higher than those in dry weather conditions. Average concentrations of nitrate and phosphate decreased slightly due to dilution and exhaustion of supply during storm events. Discharges during wet weather conditions caused deterioration of receiving water.

Keywords: Combined sewer overflows, receiving water quality, River Ecosystem classification.

Stormwater Treatment Implications: Paper presents concentration ranges for several pollutants in highway runoff.

178. **Mungur, A.S., R.B.E. Shutes, D.M. Revitt and M.A. House. "An Assessment of Metal Removal From Highway Runoff by a Natural Wetland." Water Science and Technology 32(3):169-175,(1995).**

This paper presents a preliminary assessment of the heavy metal removal performance of a natural wetland. The results are compared with the levels found in an adjacent stream which also receives runoff from the same highway. The concentrations and temporal tends of Cd, Cu, Pb and Zn in the water and sediment are discussed with the respect to the treatment efficiency of the wetland.
Keywords: heavy metals, highway runoff, wetlands
Stormwater Treatment Implications: Wetlands planted with selected species of macrophytes appear to reduce the concentration of heavy metals in highway runoff.!!

179. **Melucci, D., Gianni, G., Torsi, G, Zattoni, A., Reschiglian, P. "Experimental Analysis of Second-Order Effects on Gravitational Field-Flow Fractionation Retention of Silica Particles." Journal of Liquid Chromatography & Related Technologies, 20(16/17), 2615-2635, (1997).**

Particle size distribution analysis requires that the conversion from retention time to particle diameter is known from first principles. Hence, second-order effects must be small. Here, the focus is on the evaluation of hydrodynamic force--specifically the particle's elevation as a function of hydrodynamic effects and chemical composition of channel walls and carrier fluid. For relatively dense suspensions of silica particles (dia. 5×10^{-6} m, 0.5% w/v) inertial lift forces were negligible,
Keywords: field-flow fractionation, chemical composition, silica particles, carrier fluid.
Stormwater Treatment Implications: Outlines how field-flow-fractionation instrument is tested and calibrated with theory. Useful for laboratory analysis. Not suitable for field deployment.

180. **Muller, R.N. and Tisue, G.T. "Preparative-Scale Size Fractionation of Soils and Sediments and an Application to Studies of Plutonium Geochemistry." Soil Science, 124, 4, 191-198, (1977).**

An elutriation method, sometimes called the fluid method, is described for the fractionation of 50 g soil samples in the < 45 μm range with minimum operator involvement. Samples were dispersed in 1000mL of 0.005 M Na2CO3 and Na-oxalate (pH 9.5), stirred for 3 minutes. An initial separation was made by wet-sieving at 45 μm with a #325-mesh sieve. The suspension of < 45 μm material was pumped through a 60 mL cylinder (dia. 30 mm) at a rate of 15.4 mL/min and particles > 20 μm Stokes equivalent diameter remain in the cylinder and smaller particles are washed out. When the sample had passed through the cylinder, the material remaining was flushed with 500 mL pure dispersant at the same flowrate until the suspension cleared. Total duration of first stage separation was about 3.5 hours. The residue was separated into a 20-4 μm, 4-2 μm, and < 2 μm Stokes equivalent diameter fractions in a second run utilizing a 60 mL cylinder and a 1000

mL cylinder (dia. 70 mL) in series, with a flowrate of 0.9 mL/min. Again, the system was flushed with 1.5-2.0 L of pure dispersant. Total time for fractionation was 36 hours. Fractionation was confirmed by Coulter Counter particle size distribution measurements.

Keywords: Environmental samples, fractionation, sequential-stage elutriation, Coulter Counter.

Stormwater Treatment Implications: Technique for size fractionation of particulate samples. Not suitable for field deployment.

181.   **MacRae, V, and K.J. Hall "Comparison of Methods Used to Determine the Availability of Polycyclic Aromatic Hydrocarbons in Marine Sediment." Environmental Science and Technology, 32: 3809-3815 ,(1998).**

In this research, three methods were used to try to measure the availability of PAH from False Creek Sediment: PTD and SPMD methods. The PTD method was the most stringent assay for availability and could be useful in assessing the risk associated with exposure to a contaminated sample.

Keywords: PAHs, extraction, bioavailability, toxicity

182.   **Malo, B.A. "Partial Extraction of Metals from Aquatic Sediments." Environmental Science and Technology, 11(3): 277-282 ,(1977 March).**

Four procedures employing 0.3 M HCl, pH 3 or pH 7 citrate-dithionite, or acetic acid-hydroxylamine solutions are evaluated for their potential to remove the surface coatings from aquatic sediment particles. Ten test samples representing a range of sediment types and broad geographic distributions are examined. Data on the relative recovery efficiency of each method are reported. Selection of a procedure for use of large numbers of samples is made on the basis of recovery efficiency, limitation of structural degradation, and operational simplicity. Single operator precision data for the more efficient methods are reported.

Keywords: extraction, heavy metals, particulates

183.   **McLaren, R.G. and D.V. Crawford "Studies on Soil Copper I. The Fractionation of Copper in Soils." Journal of Science, 24(2): 172-181,(1973).**

A method for fractioning soil copper was developed and applied to 24 soils representing a range of British soil types. Correlation and regression analyses confirmed the general validity of the scheme and indicated an association between free manganese oxides and copper that considerably influences the distribution of copper between the main soil constituents. It is suggested that the concentration of copper in the soil solution is controlled by equilibria involving specifically adsorbed copper and that the bulk of the available soil copper reserves reside in the organically bound fraction.

Keywords: heavy metals, sequential extraction, bioavailability

184. Marsalek, J., Q. Rochfort, B. Brownlee, T. Mayer, M. Servos. "An exploratory study of urban runoff toxicity." Water Science Technology, vol. 39, 33-39, (1999).

Stormwater runoff was sampled from multiple storms at 14 locations in Canada. Sites represented distinct types of land use: highway, commercial, residential. The outflows of several types of BMPs were also sampled (stormwater treatment pond, constructed wetland, biofilter, oil/grit separator). Each sample was tested using a battery of four toxicity tests: Microtox, Daphnia magna, submitochondrial particle (SMP), SOS Chromotest. Overall, toxicity was present in about three fifths of the 70 samples tested. Relative test sensitivity was SMP>Daphnia>SOS Chromotest>Microtox. The greatest frequency (42% of samples) and most severe toxicity was present in runoff from multilane divided highways. Highway toxicity was predominantly present in the winter months and may have been due to contaminant accumulation in snow, mobilization of metals by chlorides, and high concentrations of road salt. Highway runoff was sampled at multiple intervals during one storm and showed evidence of a first flush effect; toxicity was only present during the first 30 minutes of runoff. Effluents from two stormwater treatment ponds showed relatively small reductions in toxicity.
Keywords: toxicity, stormwater, freshwater, stormwater pond, highway runoff, water flea, Microtox, BMP effectiveness
Stormwater Treatment Implications: Highway stormwater runoff has greater toxicity than urban runoff. Contaminant accumulation by snow and use of road salt may be important factors affecting runoff toxicity. The submitochondrial particle toxicity test is a highly sensitive test method. BMPs utilizing stormwater ponds may have limited success in reducing toxicity.!

185. Noblet, J.A., S.M. Bay, M.K. Stenstrom, I.H. Suffet. "Assessment of storm drain sources of contaminants to Santa Monica Bay. Volume VI, Task B: Toxicity of suspended solids and sediments from Ballona Creek and sediments from Malibu lagoon associated with urban stormwater runoff." University of California, Los Angeles, Environmental Health Sciences Department,(2001).

Samples of stormwater suspended solids from Ballona Creek and sediments from the mouth of Ballona Creek and Malibu Lagoon were collected in 1996 and analyzed for toxicity and contamination. Suspended solids toxicity samples were prepared by filtering the sample and then equilibrating the filter with clean seawater. Toxicity of the leachate was then measured using the purple sea urchin fertilization test. Toxicity (reduced fertilization) was present in suspended solids samples from two of three storms. Toxicity in control samples prevented assessment of toxicity in samples from the third storm. Toxicity of sediment interstitial water was also measured using the fertilization test. Interstitial water toxicity was prevalent in one of two sets of samples collected from Ballona Creek following storm events. Interstitial water toxicity was also detected in one of five samples from Malibu Lagoon collected on two occasions following storm events. Elevated concentrations of trace metals and PAHs were present in suspended solids and sediment samples from Ballona Creek. Contaminant concentrations on suspended solids were approximately five-fold

higher than sediments and were above sediment quality guidelines for biological effects (ERM) in some cases.

Keywords: Toxicity, sea urchin, suspended particles, sediment, metals, PAH.

Stormwater Treatment Implications: Contaminants associated with fine (<60 μm) stormwater particles are present in toxic amounts and forms. Sediment toxicity is associated with runoff-influenced sediments from both urbanized and relatively unurbanized watersheds.

186. **Ollivon, D., M. Blanchard, B. Garban. "PAH Fluctuations in Rivers in the Paris Region (France): Impact of Floods and Rainy Events." Water, Air, and Soil Pollution, vol. 115 (1/4), 429-444,(1999).**

Vehicle exhaust dust is found to be enriched in the PAH constituents benzo(ghi)perylene (bgp) and pyrene (pyr), and this observation is used to estimate the relative impact of car traffic and atmospheric washout on PAH levels in the rivers Seine and Marne near Paris, France. Authors estimate that during a storm event on July 1 (1995), 81% and 74% of the PAH input into the rivers Marne and Seine, respectively, were from storm flow leaching of urban surface deposits; the remainder of the PAH was contributed by rainfall.

Keywords: Flood, PAH, rainfall, river, and urban runoff

Stormwater Treatment Implications: Bgp and pyr may be useful markers of PAH contamination from vehicle exhaust dust. A large percentage of the PAH concentration in storm water runoff may be from vehicle exhaust deposited on roadways during dry weather periods, and therefore removal of particles from roadways could reduce receiving water impacts.

187. **O'Shea, M.L., R. Field. "Detection and disinfection of pathogens in storm-generated flows." Canadian Journal of Microbiology. Vol. 38, 267-276, (1991).**

This paper questions the validity of using indicator organisms (fecal coliform, total coliform, and fecal streptococcus or enterococci bacteria) to assess the disease producing potential of stormwater impacted recreational waters. A review of the literature indicates that human illness rates cannot be correlated with indicator bacterial densities in recreational waters contaminated by urban runoff. Therefore it is suggested that the total human health risk associated with the contact of recreational water be gauged by a variety of indicators including enteric and nonenteric pathogens, as well as fecal indicators whose densities can be correlated to human illness.

Keywords: storm water, disinfection, microorganisms, water-quality indicators.

Stormwater Treatment Implications: Storm generated runoff can be low in fecal indicator concentrations, yet still this runoff may have significant human disease causing potential. Hence, treatment and disinfection of stormwater prior prior to discharge could significantly improve receiving water quality.

188.   Owe, M., P. J. Craul and H. G. Halverson. "Contaminant levels in precipitation and urban surface runoff. " Water Resources Bulletin, vol. 18, 863-868, (1982).

Over the period of a year, precipitation and resultant runoff from a large shopping mall parking lot were sampled and studied in Syracuse, New York. It was found that the concentrations of contaminants Pb(0.73-2.97 mg/L), Zn(0.89-4.74 mg/L), Cu(0.12-1.38 mg/L), Cd(0.01-0.28 mg/L), and hydrocabons (3.83-19.71 mg/L) in the urban runoff were several times greater than the discharge levels generally observed in secondary treatment outfalls, and far exceed established ambient levels for receiving waters. No correlation was found between precipitation, contaminant concentration and the length of the antecedent dry period. A weak, but apparently inverse relationship was noticed between concentration and amount of precipitation. It is hypothesized that metals in parking lot runoff originated from atmospheric fallout of vehicle emissions; hydrocarbon residues were believed to be caused by vehicle leaks since none could be detected in precipitation.
Keywords: water quality, urban runoff, urban surfaces, metals, oils
Stormwater Treatment Implications: Different runoff contaminants can have different origins (e.g., atmospheric fall-out in the case of heavy metals, and vehicle leaks in the case of organic contaminants). Hence parallel and complementary management strategies may need to be adopted to control the full range of pollutants encountered in highway runoff.

189.   Peeters, E.T.H.M., T.J. De Jager, J.A.J. Beijer, A.A. Koelmans. "Effects of benzo(a)pyrene and size of organic matter particles on bioaccumulation and growth of *Asellus aquaticus*." Archives of Environmental Contamination and Toxicology, vol. 39, 307-314, (2000).

The particle size of pond sediment was manipulated to produce coarse (median diameter approx. 1,000-10,000 microns) and fine (median diameter approx. 125 microns) sediment fractions. Each sediment type was spiked with benzo(a)pyrene (B(a)P) and used in 32 day exposures to study effects on survival, bioaccumulation and growth of the isopod *Asellus aquaticus*. Each particle size group contained a similar amount of natural organic material (55%). Survival and growth of *A. aquaticus* was not affected by B(a)P in either fraction. Bioaccumulation was similar in each treatment. Isopod growth was reduced by 27% in the unspiked fine sediment fraction, indicating that size of the organic particles may have influenced food availability, food quality, or feeding behavior.
Keywords: Toxicity, PAH, isopod, bioaccumulation, sediment, bioavailability
Stormwater Treatment Implications: Sediment particles that differ in size but have a similar organic content have a similar bioavailability of PAH. Sediment-bound PAH is bioavailable and therefore potentially toxic.

190.   Pitt, R., R. Field, M. Lalor, M. Brown. "Urban stormwater toxic pollutants: assessment, sources, and treatability." Water Environment Research, vol. 67, 260-275, (1995).

Eighty seven stormwater samples from a variety of source areas in Birmingham (Alabama) were analyzed for chemical constituents and toxicity using the Microtox

assay system. Stormwater source types included parking areas, streets, and vehicle service areas. Preliminary tests using split samples showed the Microtox 100% test method yielded similar relative toxicity information when compared to a battery of approximately 20 other freshwater and marine toxicity tests. Organic contaminants (primarily PAHs) were detected in 15-20% of the stormwater samples, with the highest concentrations measured in samples from parking and vehicle service areas. Most of the organic contamination was associated with particles. Metals were almost always detected in the samples. Most of the metals concentrations were associated with particles, except for zinc, which was mostly in the dissolved phase. Toxicity was detected in 41% of the samples; parking areas contained a relatively high percentage of the toxic samples. Evaluation of potential treatment methods for stormwater showed that settling, filtration, aeration, and/or photodegradation of the stormwater produced 70-90% reductions in toxicity. Results of the treatment tests showed high variability within source types, as a result, there were no pronounced trends in treatment effectiveness between source types.

Keywords: toxicity, stormwater, highway runoff, Microtox, metals, organics, PAH, treatability.

Stormwater Treatment Implications: Toxicity of highway runoff is associated with the particulate fraction. Treatment by settling (24 hr), filtration, aeration, or photodegradation (24 hr) was effective in removing the majority of toxicity.

191. **Pickering, W.F. "Selective Chemical Extraction of Soil Components and Bound Metal Species." Critical Reviews in Analytical Chemistry, 233-263 (1981 Nov.).**

The aim of this article is to summarize the various approaches that have been adopted and to describe the chemical interactions that should be considered in any fundamental approach to the analytical problem. This review examines the current state of knowledge with respect to the relationship between (1) soil extract values and uptake of metal ions by plants, (2) the selective extraction of differently bound forms or a particular soil component, and (3) the evaluation of distribution patterns through the use of sequential extraction procedures, with appropriate emphasis on limitations, divergence of views, etc. The physical and chemical principles associated with the retention and release of metal species by various soil/sediment components are considered, and the problems associated with the development of selective extraction procedures discussed

Keywords: sequential extraction, heavy metals, bioavailability

192. **Prytula, M.T., and S.G. Pavlostathis "Extraction of Sediment-Bound Chlorinated Organic Compounds: Implications on Fate and Hazard Assessment." Water Science and Technology, 33(6): 247-254,(1996).**

Five methods were used for the extraction of hexachlorobutadiene and chlorobenzene from contaminated estuarine sediment. Analyses of wet sieved and fractionated sediment samples indicated that the contaminants are not evenly distributed throughout the sediment organic fraction but rather predominate in the larger particle sediment fraction.

Keywords: halogenated organics, extraction, particle size distribution

193. **Perdikaki, K. and C. F. Mason "Impact of Road Runoff on Receiving Streams in Eastern England Water Research, 7:1627-1633, (1999).**

Invertebrates from nine east Anglican rivers were collected to assess the pollution impact from road runoff discharges. Zinc, lead, cadmium concentrations in sediments and invertebrates did not differ significantly between sites upstream and downstream of a highway runoff discharge point. Road runoff did not appear to impact the heavy metal content of the sediments or invertebrates tested.
Keywords: highway runoff, BMPs, heavy metals, toxicity evaluation
Stormwater Treatment Implications: Road runoff is not always the dominant source of pollutants in receiving waters.

194. **Pettersson, T.J.R. "Water quality improvement in a small stormwater detention pond." Water Science Technology, vol. 38, 115-122, (1998).**

The treatment potential of a small stormwater detention pond receiving highway runoff was studied. Automated samplers were used to collect flow-weighted composites from the pond inlet and outlet during several storm events. Metal and suspended solids removal rates of 10-82% were measured for individual storms. The treatment pond did not effectively remove dissolved metals. Size of the preceding storm and the antecedent dry period were important factors influencing removal efficiency. Assessment of metal mass removal over successive storms for approximately one month yielded total removal removal efficiencies of 47-58%.
Keywords: Highway runoff, stormwater pond, BMP effectiveness, suspended particles, metals.
Stormwater Treatment Implications: Stormwater treatment ponds are effective treatment methods for removing particulate contaminants, but not dissolved contaminants. Pond capacity is a key factor in efficiency; the pond should be large enough to capture the entire amount of runoff from a storm.

195. **Pham, C.H., H.G Halverson, and G.M Heisler. "Precipitation and runoff water quality from an urban parking lot and implications for tree growth." USDA Forest Service Research Note NE, 253, (1978).**

The water quality of rainfall and runoff from a large parking lot in New Brunswick, New Jersey was studied during the early growing season, from March to June 1976. Precipitation and runoff from 10 storms were analyzed. The runoff was higher in all constituents considered, except for P, Pb and Cu. Compared with published values for natural waters, sewage effluent, and storm water drainages from urban land, the parking lot runoff was not highly polluted during the study period. However, parking lot runoff is a satisfactory source of water for urban trees.
Keyword: pollutants, urban runoff, water quality!
Stormwater Treatment Implications: Parking lot runoff can be used as a water source for certain urban vegetation.!

196. **Pitt, R., and G.W. Shawley. "San Francisco Bay Area, National Urban Runoff Project." A demonstration of non-point source pollution management on Castro Valley Creek" Report prepared for: U.S. Environmental Protection Agency. Washington, D.C. 20460 ,(1981 June).**

This report presents the results and conclusions from the EPA sponsored non-point source pollution management project on Castro Valley Creek in Castro Valley, CA. Non-point pollution in some areas represents a major obstacle to achievement of the goal of the 1972 Federal Water Pollution Control act amendments. This was the first prototype project to be part of the nationwide urban runoff program (NURP) and was designed to correlate street cleaning and urban runoff water quality.
Keywords: storm water, urban runoff, pollutants, concentrations, heavy metals!!
Stormwater Treatment Implications: Currently accepted BMP's for treating street pollution need revision since non-point pollution still represents a major obstacle to achieve the goal of the 1972 Federal Water Pollution Control act.

197. **Pratt, C. J. and J. R. W. Adams. "Sediment supply and transmissions via roadside gully pots." The Science of the Total Environment, vol. 33, 213-224, (1984).**

Reports on the input and release of pollutants in roadside gully at the Clifton Grove residential estate, Nottingham, England, between August 1976 and October 1980. The gully pots were found to represent a significant source of runoff pollutants during storms.
Keywords: Gully pot, Stormwater runoff, Sewer, Sediments
Stormwater Treatment Implications: Gully pots or stormwater catchments should be serviced periodically to prevent build-up of contaminants that can be flushed by stormwater into receiving waters.

198. **Pratt, C. J. and J. R. W. Adams. "Sediment washoff into roadside gullies." In** *Urban Stormwater Quality, Management and Planning* **(Edited by Yen, B. C.), Water Resources Publication, Colorado, U.S.A., 174-183, (1982).**

This report discusses data on the mass of material washed into roadside gullys from a Clifton Grove catchment, Nottingham during the period from August, 1979 to October 1980. A good correlation exists between the mean 14-day sediment washoff, the impervious area, maximum drainage path length, L_{max}, the slope of this length, S_{Lmax}, and the number of houses served in the catchment. Additionally the 14-day mass of sediment washoff exhibited a seasonal variation in the mass of organic debris which was moderately correlated with the estimated inflow stormwater volumes when the soil moisture deficit falls to zero. At other times when the soil moisture deficit is not zero no correlation exists between sediment washoff and the estimated inflow.
Keywords: Washoff, sediment, gullys, organic debris
Stormwater Treatment Implications: The correlation's that were found to exist between the physical parameters of the catchment and the sediment washoff should be considered in the management of stormwater runoff from residential communities.

199.   Pratt, C.J., J.D.G. Mantle, P.A. Schofield. "UK research into the performance of permeable pavement, reservoir structures in controlling stormwater discharge quantity and quality." Water Science Technology. Vol. 32, No. 1, 63-69, (1995).

Reports on storm water quantity and quality from permeable and concrete block paving surfaces with various stone types for a sub base. The studies, which were carried out at the Nottingham Trent University, UK, revealed that permeable paving surfaces trap to runoff, pollutants, and sediment, and therefore reduce receiving water quality impacts compared to traditional impermeable urban surfaces. It is estimated these permeable surfaces could remain effective for 15 to 20 years.
Keywords: Permeable pavement; concrete block; sub-base; rainfall; attenuation; pollutant retention; long-term performance.
Stormwater Treatment Implications: Permeable paving surfaces are a feasible way to reduce the contributions of road runoff pollution to the overall contamination of stormwater runoff.

200.   Rate, A.W., A.E. Robertson and A.T. Borg "Distribution of Heavy Metals in Near-Shore Sediments of the Swan River Estuary, Western Australia." Water Air and Soil Pollution, 124: 155-168, (2000).

Total Cu, Pb, Cd concentrations, and Cu, Pb, Cr, and Zn in operationally defined fractions, were determined in separate sampling events in near-shore sediments of the upper swan river estuary. Total metal concentrations in sediments were not high when compared with Australian environmental assessment guidelines for soils. Sequential extraction of sediments showed that most of the metals were in relatively immobile forms, for example bound to Fe oxides, or only extractable by aqua regia. The enhanced concentrations of Pb near storm water outfalls suggest that vehicle derived Pb may be an important contributor of Pb to the estuary.
Keyword: heavy metals, sequential extraction, bioavailability, particulate
Stormwater Treatment Implications: Lead contamination of highway runoff may have a significant impact on the quality of receiving water and sediment.

201.   Randall, C.W., K. Ellis, T. Grizzard, and W.R. Knocke. "Urban Runoff Pollutant Removal by Sedimentation." Proceeding of the Conference on Stormwater Detention Facilities, Planning, Design, Operation and Maintenance. Henniker, NH, USA. 205-219,(1982).

Reports on a laboratory study of sedimentation as a method for the removal of pollutants from urban storm water runoff. The removals of total suspended solids (TSS), COD, BOD, total organic carbon, phosphorus forms, nitrogen forms, and six heavy metals were analyzed. The particle size distribution in each sample was also determined.
Keywords: urban runoff, sedimentation, particle size distribution, pollutants
Stormwater Treatment Implications: Report presents sedimentation removal efficiencies for a number of runoff contaminants.

202. Reddy, C. M., J. G. Quinn. "Environmental Chemistry of Benzothiazoles Derived from Rubber." Environmental Science and Technology, vol. 31(10), 2847 -2853, (1997).

Benzothiazole (BT) 2-hydroxybenzothiazole (HOBT), and 2-(4-morpholino) benzothiazole (24MoBT) were detected in urban runoff, settling-pond water, urban particulate matter, road dust, and sediments. These compounds, which leach from rubber and asphalt containing 1-3% rubber, are either dissolved in water or contained in very fine tire particles.
Keywords: Water pollution, river water pollution, antifreeze, dust, benzothiazoles derived from rubber, asphalt, synthetic rubber.
Stormwater Treatment Implications: BT, HOBT, and 24MoBT may be useful molecular markers for the impact of highway runoff on receiving waters. However, these compounds are highly soluble and hence unlikely to be present in the particulate fraction of stormwater runoff or in sediments.

203. Reinertsen T.R. "Quality of stormwater Runoff From Streets." In *Urban Stormwater Quality, Management and Planning* (Edited by Yen, B. C.), Water Resources Publication, Colorado, U.S.A., (1982).

Reports on the quality of storm runoff from streets, parking lots, and sidewalks. It was found that gutter water only mobilizes 10-20% of the total mass of the contaminants deposited in a gutter. Contaminant concentrations calculated as mass/area are often higher on a side walk than a street. Residential streets and side walks were found to be less contaminated then busier streets and sidewalks. Two simple mathematical models are suggested for quick estimates of street runoff pollutant concentrations.
Keywords: urban runoff, urban surfaces, contaminants, matematical model
Stormwater Treatment Implications: Treatment or urban runoff especially from highly industrialized or developed areas is necessary to maintain reviewing water quality.

204. Ran, Y., J.M. Fu, G.Y. Sheng, R. Beckett, B.T. Hart "Fractionation and Composition of Colloidal and Suspended Particulate Materials in Rivers." Chemosphere, 41: 33-43, (2000).

A scheme for the fractionation and composition of colloidal and SPM from river waters has been tested. All for separation methods, sieving, continuous flow centrifugation, tangential flow filtration, sedimentation field flow fractionation, were for the first time used to separate five size particulate fractions from river.
Keywords: particle size distribution, particulates, particle sizing methods

205. Reschiglian, P., Melucci, D., Torsi, G. "A Quantitative Approach to the Analysis of Supermicron Dispersions by Field-Flow Fractionation with UV-Vis Detectors. The Application of an Absolute Method." Chromatographia, 44 (3/4):172-178 ,(1997).

Quantitative analysis of particle size distribution in field-flow fractionation (FFF) is required in many applications. Particle size distribution analysis in FFF requires conversion of recorded signal intensity into frequency functions of sample mass or

particle numbers. A standardless approach is presented using UV-Vis flow through spectrometer by the way of a light-obstruction model. The method requires calibration to account for effects of shape, porosity, surface composition and optical properties of the particles themselves as well as the presence of chemical species in the dispersion. The method useful for evaluating and quantifying other particle size distribution measurement techniques, e.g. light scattering.

Keywords: field-flow fractionation, particle matter analysis, calibration.

Stormwater Treatment Implications: Provides laboratory technique for verifying light scattering results and particle size distribution data from heterogeneous samples. Not suitable for field deployment.

206. SCCWRP. "Characterization of stormwater toxicity from Chollas Creek, San Diego." Southern California Coastal Water Research Project, Westminster, CA., (1999).

Composite samples of Chollas Creek stormwater from three storm events in 1999 were measured for toxicity and chemical composition. The Chollas Creek watershed is heavily urbanized, with predominantly residential land uses. Toxicity was measured using both freshwater (water flea survival & reproduction) and marine (sea urchin fertilization and mysid survival) species. Toxicity to sea urchins and water fleas were present, with the sea urchin showing the greatest degree of effect. No toxicity to mysids was detected. Toxicity identification evaluations (TIEs) determined that organophosphate pesticides (especially diazinon) were the likely cause of toxicity to the water flea (*Ceriodaphnia dubia*). Toxicity to sea urchins was due to zinc and possibly copper, however. Removal of particles from the stormwater samples did not have any effect on toxicity to the test organisms.

Keywords: Toxicity, marine, freshwater, stormwater, sea urchin, water flea, mysid, metals, pesticides, toxicity identification.

Stormwater Treatment Implications: Short-term exposure to urban stormwater produces toxicity to both freshwater and marine organisms. The cause of toxicity can be different between species, indicating that choice to test methods is critical to the answer obtained. Removal particles in stormwater is ineffective in reducing short-term toxicity because effects are due to dissolved metals or pesticides.

207. Seager, J., R.G. Abrahams. "The impact of storm sewage discharges on the ecology of a small urban river." Water Science Technology, vol. 22, 163-171, (1990).

This paper focuses on the impact storm sewage discharges (CSOs) have on the density and community structure of macroinvertebrates in an urban river in Lancashire, UK. The diversity and abundance of benthic macroinvertebrate species was reduced in areas downstream of stormwater inputs. Community structure analyses in impacted portions of the river showed a shift to favor organisms that can tolerate higher levels of pollution (e.g., oligochaetes). Temporal studies of the benthos showed changes that corresponded to stormwater discharge events. *In situ* bioassays were placed upstream and downstream of a CSO to monitor impacts associated with specific runoff events. Survival of caged amphipods was reduced at both sites in the river following a storm event, an effect that may be attributable to

physical disturbance, sediment accumulation, or contamination. Fish ventilation monitors were also used to assess *in situ* impacts of stormwater runoff. Ventilation rate of rainbow trout showed an increase during during a storm event that coincided with lowered dissolved oxygen content.
<u>Keywords:</u> Stormwater, receiving water, benthic community, in situ testing, amphipod, fish
<u>Stormwater Treatment Implications:</u> Episodic discharges of stormwater from CSOs can result in benthic community effects. In situ bioassays may be useful to observe biological responses to storm events, and may provide information for the field validation of water quality criteria obtained through laboratory bioassays.

208. **Springston, S.R., Myers, M.N., Giddings, J.C. "Continuous Particle Fractionation Based on Gravitational Sedimentation in Split-Flow Thin Cells." Analytical Chemistry. 59(2), 344-350, (1987).**

By SPLITT fractionation (SF), particles are separated parallel to the flow by an external field. An inlet and outlet splitter separates flow in into three regions: A thin upper region containing all particles, a middle, and a bottom region. Components with high mobilities must transverse the middle region in order to exit through the lower port. The method is particularly useful for separation of oversized particles. Can be coupled in series for fractionation.
<u>Keywords:</u> SPLITT field-flow fractionation, oversize particles, continuous.
<u>Stormwater Treatment Implications:</u> Demonstrates SPLITT flow field-flow-fractionation for synthetic colloids. Potentially useful for laboratory analysis. Not suitable for field deployment.

209. **Saget, G. Chebbo, M. Desbordes. "Urban discharges during wet weather: what volumes have to be treated?" Water Sci. Tech. Vol. 32, pp. 225-232,(1995).**

The authors evaluate the effectiveness of storage tanks as a means for reducing the suspended solids loads discharged from catchment basins during storms, using data collected from 17 French catchments with an average of one year of measurements. The authors do not find a first-flush effect, and they report that the basin volume needed to intercept 80% of the annual suspended solids load varies between 30 and 150 cubic meters per active ha of drainage basin.
<u>Key words</u>: stormwater runoff, particles, BMPs
<u>Stormwater Treatment Implications</u>: report provides design criteria for end-of-pipe treatment of stormwater flows for suspended solids reduction.

210. **Sansalone, J.J., S.G. Buchberger, and M.T. Koechling. "Correlations Between Heavy Metals and Suspended Solids in Highway Runoff: Implications for Control Strategies." Transportation Research Record. N1483:112-119, (1995).**

Investigates the hypothesis that heavy metal concentrations are significantly correlated to suspended solids in highway runoff. Runoff data from eight highway sites in the United States and Europe are analyzed to test this hypothesis. Results indicate a strong positive correlation between heavy metals and suspended solids.
<u>Keywords:</u> runoff, heavy metals, particle size, water quality

<u>Stormwater Treatment Implications:</u> Much of the pollution in stormwater runoff appears to be associated with particles. Hence, particle removal should be an important goal for stormwater treatment. !!

211. **Sansalone, J. J., J. M. Koran, J.A. Smithson and S.G. Buchberger. "Physical characteristics of urban roadway solids transported during rain events." ASCE J. of Environmental Engineering, vol. 124(5), 427-440, (1998).**

Lateral pavement sheet flow (LPSF) from a $300m^2$ area of Interstate 75 in Cincinnati was sampled during 13 separate storms in 1995-97. Samples of LPSF collected over the course of each storm were analyzed for TSS, VSS, TDS, VDS, and COD, and PSD; the event mean concentrations for these parameters (excluding PSD) were 130.7 mg/L, 41.6 mg/L, 158.4 mg/L, 80.8 mg/L, and 229.7 mg/L, respectively. Authors divided storm events into low and high runoff volume events. In the former, TDS and TSS were released continuously over the course of the storm, presumably because of large vehicle to runoff volume ratios. In the latter, TDS and TSS were released primarily at the beginning of the hydrograph. The authors refer to these two different cases as "mass limited" and "flow limited." The effect of antecedent dry period is also noted. The PSDs are remarkably similar across storm events; these curves appear to be generated by sieve analysis as there are no particles smaller than 25 microns. Perhaps the most interesting result in this paper is the measurement of specific surface area (SSA) as a function of particle size. Remarkably, the measured SSA values are 1000 times larger than what would be estimated if the particles were spheres. Particles released from the highway must have significant internal porosity. Most of the SSA is associated with particles in the 425 to 850 micron size ranges.
<u>Keywords:</u> Environmental transport, Particle size, Runoff, Water pollution, Physical characteristic roadway solid transported rainwater.
<u>Stormwater Treatment Implications:</u> Particles released from a highway during storms have very large SSA values (1000 times greater than predicted for spherical particles), and hence these particles are capable of carrying significant adsorbed loads of pollutants. Most of the surface area is associated with the 425 to 850 micron size ranges, so this might be the best size range to target for removal. The release of solids during a storm exhibited first flush, so treatment of the initial portion of the hydrograph is important.

212. **Sansalone, J. and S. Buchberger. "Partitioning and First Flush of Metals in Urban Roadway Stormwater." Journal of Environmental Engineering, 123(2):134-143,(1997 Feb).**

Storm water runoff from urban roadways often contains significant quantities of metals and solids generated mainly from traffic related activities. Metals partition into dissolved and particulate-bound fractions as a function of pH, pavement residence time, and solids concentration. Results indicate that Zn, Cd and Cu are mainly in dissolved form while Pb, Fe and Al are mainly particulate bound.
<u>Keywords:</u> urban runoff, storm water, metals, particulate fractions, dissolved fraction
<u>Stormwater Treatment Implications:</u> The high concentration of dissolved Zn, Cd, and Cu found in LPSF suggests that removal of particles alone may be insufficient

for reducing metal toxicity of highway runoff. Strategies to immobilize these metals might include adsorption, ion exchange, and/or precipitation. Infiltration of runoff containing high levels of dissolved metals could negatively impact groundwater quality.

213.   Sansalone, J.J. and S.G. Buchberger. "Partitioning and First Flush of Metals in Urban Roadway Storm Water." ASCE J. of Environmental Engineering, vol. 123(2), 134-143, (1997).

Lateral pavement sheet flow (LPSF) from an experimental site on Interstate 75 in Cincinnati was sampled during five rainfall runoff events in 1995 and analyzed for metals and solids. Results indicate that Zn, Cd, and Cu are mainly dissolved while Pb, Fe, and Al are mainly particulate-bound. Dissolved metals exhibit a strong first-flush; the fraction of dissolved metals increased with decreasing rainfall pH and increasing average pavement residence time (APRT). Event mean concentrations of Zn (459-15,244), Cd (5-11), and Cu (43-325) exceed surface water quality discharge standards. Also includes a nice summary figure showing highway sources of different inorganic and organic pollutants.
Keywords: metals, pavement sheet flow, runoff, solids
Stormwater Treatment Implications: The high concentration of dissolved Zn, Cd, and Cu found in LPSF suggests that removal of particles alone may be insufficient for reducing metal toxicity of highway runoff. Strategies to immobilize these metals might include adsorption, ion exchange, and/or precipitation. Infiltration of runoff containing high levels of dissolved metals could negatively impact groundwater quality.

214.   Sansalone, J.J., K.P. Paris, S.G. Buchberger. "Heavy Metals in the First-Flush of Highway Nonpoint Pollutants."International Water Resources Engineering Conference Proceedings. Proceedings of the 1st International Conference on Water Resources. Part 2 (of 2). San Antonio, TX, USA.

The concentrations of several metals, and their partitioning between dissolved and particulate phases, were measured in first-flush urban highway runoff. Use of a first-order expression for modeling metal washoff is examined.
Keywords: highway runoff, heavy metals, particle size, particulate fraction, particle size distribution
Stormwater Treatment Implications:!!Mathematical modeling of stormwater contamination is potentially a powerful tool in runoff management.

215.   Sansalone, J.J. and S.G. Buchberger. "Characterization of solid and metal element distributions in urban highway stormwater." Water Science Technology, vol. 36, 155-160, (1997).

This paper presents field data on the particle size distributions and metal contaminants present in storm water runoff and snow melt at an urban highway site in Cincinnati, Ohio. Metal element analysis on the particle size distributions indicate that the concentration of Zn, Cu, and Pb (in micrograms per gram of solid) increase

with decreasing particle size; Cd concentrations did not show any clear trends with respect to particle size.

Keywords: Highway runoff, metal elements, particle size distributions (PSDs), specific surface area (SSA), partitioning.

Stormwater Treatment Implications: BMPs that remove small particles (<250 microns) may be more effective at treating runoff for metal contaminants.

216.   **Sansalone, J.J., S.G. Buhberger "An Infiltration Device as a Best Management Practice for Immobilizing Heavy Metals in Urban Highway Runoff." Water Sci. Technol., 32(1, Innovative Technologies in Urban Storm Drainage), 119-25, (1995).**

This paper analyzes metal and suspended solid data collected in the U.S. during the 1980s for the Federal Highway Adminstration (FHWA) and from a Jessheim, Norway roadway. Authors report that the event mean concentrations (EMC) of metals (Cu, Pb, Zn, Fe) are highly correlated with snow washoff, long duration rainfall events, and with particles smaller than 15 μm. Surprisingly, there is a poor correlation between metals and suspended solids concentration for most stormwater runoff events.

Keywords: Highway runoff; suspended solids; underdrains; partial exfiltration trench; infiltration; best management practices; first-flush.

Stormwater Treatment Implications: Authors suggest that partial exfiltration trenches (PET) may be a good management tool for treating highway runoff because: i) their geometry is compatible with the linear nature of highways, ii) they have several modes of treatment that will capture different types of pollutants, including surface straining of large debris, deep bed filtration of small particles, and direct sorption of dissolved metals and organics. Possible disadvantages of PET include maintenance costs and construction costs, and the possible contamination of shallow groundwaters by heavy metal breakthrough. Paper also includes two tables, which summarize the features of primary BMPs for highway runoff treatment.

217.   **Sartor, J.D. and G.B. Boyd. "Water pollution aspects of street surface contaminants." EPA Report EPA-R2-72-081, November, (1972).**

This excellent report reviews the state-of-the-art as of 1972; remarkably, many of the conclusions in the report presage journal articles published almost thirty years later. Based on data presented in the report, the authors estimate that, for a typical city of 100,000 people, the pollutant load in street runoff generated in the first hour of a moderate-to-heavy storm exceeds the sanitary sewer pollutant load with respect to settable and suspended solids (560,000 vs. 1,300 lb/hr in runoff and raw sewage, respectively), BOD5 (5,600 vs. 1,100 lb/hr), COD (13,000 vs. 1,200 lb/hr), Kjeldahl nitrogen (880 vs. 210 lb/hr), and phosphates (440 vs. 50 lb/hr). Even the total coliform levels in storm water exceed secondarily treated sewage by three orders of magnitude (4000×10^{10} vs. 4.6×10^{10} organisms/hr). The quantity and character of contaminants found on street surfaces is summarized in the report by Tables 47 and 48. On a mass basis, the major constituent of street surface contaminants is inorganic in nature and similar to common sand and silt. However, high levels of oxygen demand, nutrients, heavy metals, pesticides, and coliform are also reported. Of the

heavy metals, Zn and Pb are generally present at higher concentrations compared to Cr and Ni. The high levels of Pb may be related to the prevalence, at the time, of leaded gasoline. The speciation of these metals (e.g., redox state, complexation with organic and inorganic compounds) was not known, but presumed to be important relative to the metals' reactivity, toxicity, and environmental mobility. Report also includes a good summary of the environmental impact of different contaminants. The pollutant load washed from a street during a storm increases with increasing contaminant loading intensity. In turn, contaminant loading intensity is affected by surrounding land-use (industrial>residential>commercial), elapsed time since the streets were last cleaned either intentionally or by rainfall, local traffic volume and character, street surface type and condition, public works practices, and season of the year. Organic contaminants accumulate on road surfaces faster than inorganic contaminants. Solids are concentrated along the edge of the roads or in road gutters; street sweeping is inefficient at removing the smallest particles, and instead redistributes them over the street. The rate at which particles are removed from streets was found to follow a simple first-order rate expression. The first order rate constant k (units of hr/in./min) depends upon street surface characteristics but was found to be almost independent of particle size (from 10 to 1000 microns). Street surface characteristics were found to exert a strong influence on the value of k. Asphalt streets had loadings about 80% heavier than all concrete streets; streets in fair-to-poor condition had loadings about 2.5 times as high as streets in good-to-excellent condition. A large portion of the overall pollutant load is associated with the fine solids fraction of the street surface contaminants. While they harbor most of the pollutants, these fine particles constitute a small fraction of the overall solids mass released from roads during a storm. The very fine silt-like material (<43 microns) accounts for only 5.9% of the total solids but 1/4 of the oxygen demand, 1/3-1/2 of nutrients, 1/2 of heavy metals, and 3/4 of total pesticides. Because of metal toxicity, COD is a better measure of oxygen demand than BOD5 in storm water runoff. Street sweeping is inefficient at removing the smallest particles where most of the pollutants reside (15% removal for particles <43 microns), and hence this BMP is useful primarily for aesthetic purposes. Catch basins are reasonably effective in removing coarse inorganic solids from storm runoff (coarse sand and gravel) but are ineffective in removing fine solids and most organic matter. Finally, the report provides a nice summary of the transport pathways taken by roadway contaminants.

Keywords: Sewage wastes, water pollution, stormwater runoff, street cleaning, pavements, roads, stormwater pollution.

Stormwater Treatment Implications: While some modest improvement in pollutant removal can be achieved using well designed street sweeping programs and catch basins, the report concludes that diverting storm water runoff to the sanitary sewer system may be the best strategy for reducing receiving water impacts of stormwater runoff.

218. **J. D. Sartor, G.B. Boyd, F.J. Agardy. "Water pollution aspects of street surface contaminants." Journal Water Poll. Control Fed. Vol. 46, 458-467, (1974).**

This article is essentially a summary of the findings reported in the EPA report authored by Sator and Boyd, and summarized at length in this appendix. The major conclusions are that storm water runoff is highly contaminated, in some cases as bad or worse than municipal sewage. A very large percentage of the contaminants (up to half of the heavy metals) are associated with the finest particles, which constitute a minority of the total particle mass on road surfaces. The majority of the material on road surfaces is inorganic particles. Authors present an exponential relationship for the rate at which particles are washed off the road surface during a rain event. See the EPA report review for a more detailed description of their results.
<u>Key Words</u>: Heavy metals, stormwater runoff, first flush.
<u>Stormwater Treatment Implications</u>: Most of the pollutants in storm water runoff are associated with the finest particles, implying that most of the treatment should focus on the small end of the size spectrum. Further, traditional street sweeping operations are useful only for aesthetic purposes—they are not effective at reducing the pollutant load during storms.

219. **Shaheen, D. G. "Contributions of Urban Roadway Usage to Water Pollution." Environmental Protection Agency Report No. 600/2-75-004. U.S. Government Printing Office, Washington D.C., (1975).**

This investigation was undertaken in Metropolitan Washington, D.C., to determine the role that street surface contaminants play when carried into receiving waters by storm runoff. It was found that motor vehicular traffic is directly or indirectly responsible for deposition of substantial quantities of materials on roadways in urban areas. Significant levels of toxic heavy metals, asbestos, and slowly biodegradable petroleum products and rubber are deposited directly from motor vehicles along with large quantities of particulate materials contributed indirectly by traffic. The particulates contributed indirectly by traffic are largely inorganic, but have associated with them solids and nutrients which represent a serious source of water pollutants in all metropolitan areas. It was determined that these contaminants constitute a substantial portion of the overall water pollution problems of cities.
<u>Keywords:</u> Runoff, particles, roadway, deposition heavy metals, traffic.
<u>Stormwater Treatment Implications:</u> The contribution of streets surface pollution to the overall pollution loadings is significant, therefore it must be treated and/or reduced.

220. **Shinya, M., T. Tsuchinaga, M. Kitano, Y. Yamada and M. Ishikawa "Characterization of Heavy Metals and Polycyclic Aromatic Hydrocarbons in Urban Highway Runoff." Water Science and Technology, 42(7-8): 201-208, (2000).**

Urban highway runoff samples collected from four rainfall drains were analyzed for heavy metals and polycyclic aromatic hydrocarbons (PAHs). The concentrations of constituents varied widely during the time history of each storm and appeared to be highest in the first runoff water. Results showed that iron and aluminum were the

principal constituents in the particulate fraction. Cadmium, chromium, copper, manganese, lead and zinc were mainly particulate-bound while nickel was mainly in dissolved form.
Keywords: highway runoff, heavy metals, PAHs, particulates, dissolved fraction, particulate fraction, toxicity evaluation
Stormwater Treatment Implications: Treatment of first-flush runoff only may be an economically feasible way to reduce the adverse effects of highway runoff.

221.   **Shutes, R.B.E., Revitt, D.M. Revitt, I.M. Lagerberg, V.C.E. Barraud. "The design of vegetative constructed wetlands for the treatment of highway runoff." The Science of the Total Environment. Vol. 235, 189-197, (1999).**

This paper presents an assessment, motivated by the Environment Agency for England and Wales, of constructed wetlands as a possible treatment system to minimize the effects of highway runoff on local receiving waters. It was found that a constructed wetland can be designed to effectively treat first flush runoff or, if space is not limited, to treat highway runoff for the duration of the storm. Design and maintenance considerations and suggestions, such as ideal reed and plant species, bed gradient, and maintenance time periods are presented.
Keywords: Constructed wetlands; runoff; water quality; maintenance; oil separator.
Stormwater Treatment Implications: Wetlands may be a feasible way to treat stormwater, if they can be properly maintained and space is not severely limited.

222.   **Scherger, D., and J. Davis. "Control of Stormwater Runoff Pollutant Loads by a Wetland and retention Basin". International Symposium on Urban Hydrology, Hydraulic and Sediment Control, University of Kentucky, Lexington, Kentucky-July 27-29, (1982).**

This study determined the operational costs and effectiveness of two types of best management practices (BMP's) in the reduction of pollutant loads present in urban stormwater runoff. The information presented in this paper represents the efforts of a two year sampling program.
Keywords: pollutants, storm water runoff, wetlands, retention basin, BMP
Stormwater Treatment Implications: Constructed wetlands are a useful management tool for reducing pollutant loads in stormwater runoff. !!

223.   **Shelley, P., and D. Gaboury. "Estimation of Pollution from Highway Runoff-Initial Results". Impact and Quality Enhancement Technology, Proceedings of an Engineering Foundation Conference. Henniker, NH, USA: 459-473.**

Reports on the Federal highway Administration (FHWA) of the United States Department of Transportation's research program to characterize stormwater runoff from highways, assess its impacts on receiving waters, and determine the effectiveness of various control measures. As a part of this research program, a contractor team has been tasked with developing models that could be used by planners and highway engineers for predicting pollutant runoff loads from highways.
Keyword: highway runoff, pollutants, urban runoff, water quality, methodology
Stormwater Treatment Implications: Effective modeling tools could significantly aid the design of highway runoff treatment systems.

224. **Shelley, P.E., E.D. Driscoll and J.D. Sartor. "Probabilistic Characterization of Pollutant Discharges from Highway Stormwater Runoff." Science of the Total Environment, 59:401-410,(1987).**

This paper presents the preliminary results of a project aimed at developing models that can be used by planners and highway engineers for predicting pollutant runoff from highways. A brief review of different approaches to predicting pollutant runoff loads from highways is followed by a description of the database being assembled as a part of this project.
Keywords: highway runoff, pollutants, analysis, methodology
Stormwater Treatment Implications: Effective modeling tools could significantly aid the design of highway runoff treatment systems.

225. **Simpson, D.E. "Urban Runoff Pollution Research in Natal." Natal Town and Regional Planning Supplementary Report, 37 ,(1992).**

Due to rapid population growth and continued industrial expansion in the RSA there is an urgent need to protect limited water resources from pollution carried by storm water runoff in urban areas. It is therefore necessary to assess the types and amounts of pollutants derived from different urban land-uses. Three catchments have been studied. This report synthesizes data collected in these catchments for periods of one, two and three years respectively.
Keywords: runoff, urban, loads, water quality.
Stormwater Treatment Implications: End-of pipe treatment facilities, such as detention/retention systems may be more effective for particle-bound pollutants, and less effective for soluble. Wetlands improve runoff quality by a combination of physical, chemical and biological processes.!!

226. **Stotz, G. "Documentation of Highway Surface Runoff in the FRG". Science of the Total Environment, 93:507-514 (1990).**

In the past, detention basins along highways were considered necessary only when the highways passed through water resources conservation areas. Recently, however, it has been recognized, that in order to protect water resources, basins must be constructed to contain the many toxic pollutants in surface water runoff from roads. In this report, the efficiency of three different types of basins were investigated. When properly dimensioned, a detention basin can discharge an effluent in which the concentrations of hazardous substances, originating from motor vehicle traffic, have been reduced by 50% to 80% through sedimentation and separation processes.
Keywords: highway runoff, pollutants, heavy metals, BMPs.
Stormwater Treatment Implications:!Sedimentation basins are particularly effective management tools for removing pollutants from stormwater.!

227. **Stotz, G. "Investigation of the Properties of the Surface Water Runoff From Federal Highways in the FRG." Science of the Total Environment, 59:329-337, (1987).**

Street soil originating from motor vehicle traffic, winter highway maintenance, and atmosphere fallout can cause pollution of surface waters during storms. A set of studies are described in which water quality testing was carried out on stormwater

runoff samples from three federal highways with heavy traffic in the years from 1978-1981.
Keyword: highway runoff, heavy metals
Stormwater Treatment Implications:!!Extensive water quality monitoring of stormwater runoff is a necessary prerequisite for the development of effective BMPs.

228.   Thomson, N.R., E.A. Mcbean, W.Snodgrass and I.B. Monstrenko. "Highway Storm Water Runoff Quality: Development of Surrogate Parameter Relationships." Water, Air, and Soil Pollution, 94:307-347,(1997).

Regression-based relationships are derived for predicting pollutant loading from highways during storms. The objective is to identify a subset of constituents that can be used as valid measure of pollutant levels in highway runoff.
Keywords: highway runoff, pollutants, concentrations
Stormwater Treatment Implications:!Identification and detection of surrogate parameters could significantly reduce the number of water quality parameters that need to be measured to evaluate pollutant loads in highway runoff.

229.   Tessier, A., P.G.C. Campbell, and M. Bisson "Sequential Extraction Procedure for the Speciation of Particulate Trace Metals." Analytical Chemistry, 51(7): 844-851,(1979 June).

An analytical procedure involving sequential chemical extractions has been developed for the partitioning of particulate trace metals (Cd, Co, Cu, Ni, Pb, Zn, Fe, and Mn) into five fractions: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual. Experimental results obtained on replicate samples of fluvial bottom sediments demonstrate that the relative standard deviation of the sequential extraction procedure is generally better than $\pm 10\%$. The accuracy, evaluated by comparing total trace metal concentrations with the sum of the five individual fractions, proved to be satisfactory. An application of the proposed method to river method to river sediments is described, and the resulting trace metal speciation is discussed.
Keywords: sequential extraction, heavy metals, particulates.

230.   U.S. Environmental Protection Agency. "Method 3050B Acid Digestion of Sediments, Sludges, and Soils." Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, SW-846. 3rd ed., (1992).

Two separate digestion procedures are summarized one for the preparation of sediments, sludges, and soil samples for analysis by flame atomic absorption spectrometry (FLAA) or inductively coupled plasma atomic emission spectrometry (ICP-AES) and one for the preparation of sediments, sludges, and soil samples for analysis of samples by Graphite Furnace AA (GFAA) or inductively coupled plasma mass spectrometry (ICP-MS).
Keywords: heavy metals, methodology, solid fraction!

231. U.S. Environmental Protection Agency. "Method 3051 Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils." Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, SW-846. 3rd ed., (1992).

This method is an alternative to Method 3050. It provides rapid multi-element acid l each digestion prior to analysis.
Keywords: heavy metals, methodology, solid fraction!

232. U.S. Environmental Protection Agency. "Method 3545 Pressurized Fluid Extraction (PFE)." Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, SW-846. 3rd ed., (1992).

This procedure is an alternative to Soxhlet extraction for extracting water insoluble or slightly water-soluble semivolatile organic compounds from soils, clays, sediments, sludges, and waste solids. The method uses elevated temperature (100EC) and pressure (1500 - 2000 psi) to achieve analyte recoveries. It uses less solvent and time than the Soxhlet extraction. The total mass of material to be prepared is usually 10 to 30 g of material are usually necessary, which is very large for suspended sediment.
Keywords: organics, methodology, solid fraction, extraction!!

233. U.S. Environmental Protection Agency. "Method 3550B Ultrasonic Extraction." Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, SW-846. 3rd ed., (1992).

This procedure is for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The method is divided into two sections, based on the expected concentration of organics in the sample. The low concentration method (<20 mg/kg) uses a larger sample size and a more rigorous extraction procedure (30g). The medium/high concentration method (>20 mg/kg) is much simpler, faster, and uses only 2 g samples.
Keywords: organics, methodology, solid fraction, extraction!!

234. U.S. Environmental Protection Agency. "Method 3561 Supercritical Fluid Extraction of Polynuclear Aromatic Hydrocarbons." Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, SW-846. 3rd ed., (1992).

This method uses supercritical fluids for the extraction of polynuclear aromatic hydrocarbons (PAHs) from soils, sediments, fly ash, solid-phase extraction media, and other solid materials which are amenable to extraction with conventional solvents.
Keywords: organics, methodology, solid fraction, extraction!!

235. U.S. Environmental Protection Agency. "Method 3540C Soxhlet Extraction." Test Methods for Evaluating Solid Waste - Physical/Chemical Methods, SW-846. 3rd ed., (1992).

This procedure is used for extracting nonvolatile and semivolatile organic compounds from solids such as soils, sludges, and wastes. The Soxhlet extraction process ensures intimate contact of the sample matrix with the extraction solvent. This method is applicable to the isolation and concentration of water-insoluble and

slightly water soluble organics in preparation for a variety of chromatographic procedures. For this test, 5 to 10 g of material is required, which is very large for suspended sediment.
Keywords: organics, methodology, solid fraction, extraction.

236. **U.S. Environmental Protection Agency "Guidance Specifying Management Measures for Sources of Nonpoint Pollution in Coastal Waters." EPA-840-B-93-001c, (1993 January).**

A comprehensive technical document on methods to abate and control nonpoint pollution in coastal areas. Primarily intended for State and local watershed project staff.
Keywords: BMP, pollutants, water quality

237. **U.S. Environmental Protection Agency. "EPA's Contaminated Sediment Management Strategy" EPA-823-R-98-001, (April 1998).**

Reports on EPA's strategy for managing contaminated sediments. Future research needs include numerical assessment guidelines to evaluate contaminant concentrations, and standardized bioassay tests to evaluate the bioaccumulation and toxicity potential of specific sediment samples.
Keywords: contaminated sediments, standards, bioassay testing!

238. **Verbank, M.A. "Identification of the depth dependent transportation of particulate solids in dry weather sewage flows."** *Proc., 6th Int. Conf. on Urban Storm Drainage*, **Ontario, Canada ,(1993).**

Reports on the suspended solid concentration profile in dry weather sewage flows, in Brussels, Belgium. The concentration profile increases with depth, from approximately 220 mg/L at the surface to about 280 mg/L 0.15 m above the sediment bed; a sharp decrease in the suspended solid concentration occurs in the last 0.15 m of the water column, from about 280 mg/L to about 260 mg/L. The velocity profile of the water decreased with depth, from about 0.6 m/s at the surface to about 0.4 m/s near the bottom.
Keywords: Sewer sediment, combined sewers, suspended solids, concentration profile
Stormwater Treatment Implications: Further identification and understanding of the sedimentation and bed load transport mechanisms will allow the design of new management strategies for reducing suspended solids concentrations in stormflows, and for reducing the cleaning costs of combined sewers.

239. **Verbank, M.A. "Capturing and releasing settleable solids—The significance of dense undercurrents in combined sewer flows." Water Science and Technology, vol. 31(7), 85-93, (1995).**

In Brussels, Belgium the "first flush" effect of a low-sloped combined sewer was investigated. The apparent first flush was not a result of the resuspension of previously deposited sediments, but a dynamic component of the sewage flow itself. During low flow periods, organic debris (e.g., human and food wastes) settles to form a dense undercurrent with a lower velocity than the main flow. It was found

that this undercurrent collapses and subsequently releases its contained polluting material into the entire water column when the shear forces near the bottom exceed 1.1-1.2 N/m^2.

Keywords: Combined sewer; inner layer; organic matter; sanitary sewage; settleable solids; shear stress; storm overflow; suspended load; resuspension.

Stormwater Treatment Implications: With the low shear value required to induce an artificial flush, sewer networks could be flushed during key hours in order to convey the highly polluting material to appropriate treatment facilities.

240.   Viklander, M. "Particle size distribution and metal content in street sediments" ASCE J. of Environmental Engineering, vol. 124, 761-766, (1998).

Study presents data on the PSD and metal content of street sediment left by snow melt. A conventional street sweeper was used to collect sediment samples in two areas, one in the center of Lulea, Sweden, and another in a housing area. Within each of these areas, low and high traffic sites were selected. The amount of sediment increased with traffic intensity, and sites with sidewalks had more solids and were depleted in smaller particles. For all sites without sidewalks, the PSDs were similar. With few exceptions most of the heavy metals were present in the smallest size fraction (<75 microns). The metals leached from the sediments in the following order: Cd>Zn>Cu>Pb.

Keywords: Roadway sediments, snow, metals, PSDs

Stormwater Treatment Implications: The majority of metals are associated with the smallest size fractions, and hence treatment methods may need to target these small particles.

241.   Willemsen, G.D., H.F. Gast, R.O.G. Franken, J.G. M. Cuppen. "Urban storm water discharges: effects upon communities of sessile diatoms and macro-invertebrates."Water Science Technology, vol. 22, 147-154, (1990).

This study examined the effects of urban stormwater discharge on benthic diatoms and macro invertebrates in freshwater receiving waters in the Netherlands. Effects of urban stormwater discharge on communities were expressed by different composition of species at discharge sites. There was a high abundance of *Chironomus* spp., *Psectotanypus varius*, Tubificidae, and Culicidae in stagnant receiving waters. These organisms are often indicative of organic pollution and disturbance. Animals more sensitive to pollution, such as Odonata, Trichoptera, Gammaridae and Ephemeroptera, were found mainly in the reference waters and were mostly absent from receiving waters. Impacts near CSOs were greater than the effects of discharges from separate sewer systems. Benthic diatoms appeared to be more sensitive to water quality variations than macroinvertebrates. There were no pronounced differences in the number of taxa at the three sites in the running waters.

Keywords: Stormwater, benthic community, freshwater, diatom, invertebrate, receiving water

Stormwater Treatment Implications: Stagnation of stormwater and organic enrichment can result in degraded benthic communities. Benthic community analysis is a sensitive indicator of degraded habitat quality.

242. **Wimberley, F.R., and T.J. Coleman. "The Effect of Different Urban Development Types on Stormwater Runoff Quality: A Comparison Between Two Johannesburg Catchments." Water S.A. 19(4):325-330, (1993 Oct.).**

Field data from two catchments suggest that the type of development within a catchment, and the level of management of engineering services, can affect the quality of urban stormwater runoff.
Keyword: urban runoff, pollutants!!
Stormwater Treatment Implications: The type of development within an urban watershed will determine the type of stormwater treatment necessary to provide the receiving bodies of water with significant protection.

243. **Wyatt, P.J. "Submicrometer Particle Sizing by Multiangle Light Scattering following Fractionation." Journal of Colloid and Interface Science, 197(1), 9-20, (1998).**

Verification of field-flow fractionation (FFF) efficiency using multi angle light scattering (MALS). The MALS/FFF combination provides some advantages relative to FFF, photon correlation spectroscopy, and capillary hydrodynamic chromatography techniques used alone. For many classes of particles, resolution of the MALS/FFF combination far exceeds that of TEM measurements.
Keywords: field-flow fractionation, particle size analysis, multi-angle light scattering, static light scattering.
Stormwater Treatment Implications: Laboratory technique for size fractionation and particle size analysis. Not suitable for field deployment.

244. **Weltens, R., R. Goossens, S. Van Puymbroeck. "Ecotoxicity of contaminated suspended solids for filter feeders (*Daphnia magna*)." Archives of Environmental Contamination and Toxicology, vol. 39, 315-323, (2000).**

The bioaccumulation and toxicity of copper and zinc bound to particles was studied. Four types of particles (clay, sand, peat, and algae) were spiked with metals and then used in 48-hr. survival tests with *D. magna*. Dissolved and particulate metal concentrations were measured for each treatment. Particulate concentrations of 200-500 mg/L were used in the experiments. Exposure to unspiked particles (500 mg/L) did not produce toxicity. Mortality was present in experiments with spiked clay, peat, and algae. Toxic effects were due to the ingestion and assimilation of metal from the particles as the dissolved phase metal concentrations were below toxic levels. The sand treatment did not cause the expected toxicity, however. This result was probably due to an inhibitory effect of the sand on filter feeding activity by *D. magna*. Experiments were conducted using both static and flow-through exposure systems. Greater toxicity was measured in the flow-through system, probably because water motion maintained the particles in suspension where they could be ingested by the test organisms.
Keywords: toxicity, suspended particles, metals, water flea, bioavailability
Stormwater Treatment Implications: Sediment-associated metals may be bioavailable and a source of toxicity to filter feeding or deposit feeding aquatic life. The organic carbon content of the particles does not have a strong effect on bioavailability in laboratory experiments.

245.   Yamane, A., I. Nagashima, T. Okubo, M. Okada and A. Murakami. "Storm
        Water Runoff of Hydrocarbons in the Tama River Basin in Tokyo (Japan) and
        Their Fate in the River." Water Science and Technology. 22(10/11):119-126 ,
        (1990).

Storm water runoff pollution in urban areas has a significant impact on the aquatic
environment. The Nogawa River, which is a tributary of the Tama River in Tokyo,
runs through a residential district. At high water levels, more aliphatic hydrocarbons
were found in the river water than at normal water levels. It seemed that the
hydrocarbons in the water at normal water levels originated from gray water, and
those at high water levels were from automobile emissions and/or resuspended
bottom sediment. Concentrations of polycyclic aromatic hydrocarbons (PAHs) were
negligible in river water at both normal and high water levels whereas they were
high in the bottom sediment. It is probable that the PAHs originated from sources
other than automobile emissions
Keywords: storm water; urban runoff; aliphatic hydrocarbons, polycyclic aromatic
hydrocarbons, roadside dust; bottom sediment!
Stormwater Treatment Implications:!!Treatment of certain pollutants such as PAHs
may need to be a continuous process as they are resuspended from the sediment.

246.   Yousef, Y.A., T.Hvitved-Jacobsen, M.P. Wanielista, and H.H. Harper
        "Removal of Contaminants in Highway Runoff through Swales." The Science of
        the Total Environment, 59: 391-39,(1987).

Simulated highway runoff was pumped over a well-established grassy swale.
Dissolved metal concentrations, particularly ionic species, were better removed than
phosphorus and nitrogen. Nutrient concentrations in highway runoff flowing over
roadside swales may actually increase.
Keywords: highway runoff, pollutants, heavy metals, BMPs, swales
Stormwater Treatment Implications: It is recommended that swales alone should not
be used for management of highway runoff, unless the effluent is channeled to more
appropriate treatment units such as a retention/detention system.

247.   Yousef, Y.A., H.H.Harper, L.P. Wiseman, and J.M. Bateman "Consequential
        Species of Heavy Metals in Highway Runoff." Transportation Research Record:
        56-62; ISSN: 0361-1981 ,(1985).

Speciation of heavy metals in aquatic systems plays a key role in their transport,
chemical reactions, and bioavailability. Physical and chemical species that may
cause significant consequences, known as consequential species, should be identified
before the potential environmental impact of the metal is determined. Species of
dissolved lead, zinc, copper, and cadmium were identified using anodic stripping
voltametry for rainfall, highway and bridge runoff.
Keywords: heavy metals, highway runoff, water quality, storm water runoff
Stormwater Treatment Implications: Identification of heavy metal species and the
potential environmental impact that they pose, could be an invaluable tool in the
development of an effective stormwater control strategy.

248. **Yousef, Y.A., M.P. Wanielista, and H.H.Harper. "Removal of Highway Contaminants by Roadside Swales." Highway Pollution, Proceedings of the Second Intl. Symposium, London, England, 391-399, (Jul 7-11, 1986).**

Removal of highway contaminants by roadside swales was investigated. Runoff from highway and grassy swale areas were collected for eight months. Also, a controlled water flow from adjacent detention/retention ponds was dosed with nitrogen, phosphorus, and heavy metals to produce concentrations typical of highway runoff.
Keywords: highway runoff, swales, heavy metals, BMPs, pollutants
Stormwater Treatment Implications: Removal of heavy metals may be caused by precipitation and sorption processes. Therefore, charged ions and complexes may be removed more efficiently than stable complexes and non-charged particles.

249. **Yeoman, S., Sterritt, R.M., Rudd, T, Lester, J.N. "Particle Size Fractionation and Metal Distribution in Sewage Sludges." Water, Air, and Soil Pollution, 45, 27-42, (1989).**

A sequential step filtration technique was used to fractionate raw, activated, and settled sewage sludge samples. Sample size was 150 mL of sludge; sample concentration not specified. Seven filter pore sizes were used: 100, 53, 20, 8 microns (mesh type, Henry Simon Ltd, Stockport, Cheshire), 2.5 mm (cellulose filter, Whatman No. 42, BDH Ltd., UK), 0.45, and 0.2 microns (Cellulose acetate, Amicon, Ltd., UK). No confirmation of final particle size distribution was performed.
Keywords: Environmental samples, fractionation, sequential-stage filtration, model.
Stormwater Treatment Implications: Technique for size fractionation of particulate samples. Not suitable for field deployment. Not recommended for laboratory use.